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<b>(54) Title:</b> RELAXOR FERROELECTRIC SINGLE CRYSTALS FOR ULTRASOUND TRANSDUCERS		
<b>(57) Abstract</b>		
<p>&lt;001&gt; oriented crystals of lead zinc niobate – lead titanate solid solution (0 to 5 mole % lead titanate) have high electromechanical coupling &gt; 85 % and exhibit electric field induced phase transition at electric field levels &gt; 10 x Ec (where Ec is the coercive field), resulting in increased transducer driving voltages, decreased fabrication degradation, and high sensitivity/large bandwidth transducer characteristics due to high electromechanical couplings, up to 92 %. &lt;001&gt; oriented crystals of lead magnesium niobate – lead titanate solid solution (20 to 50 mole % lead titanate) also exhibit high electromechanical couplings &gt; 85 % and up to 94 %, and thereby can be formed into transducers which exhibit both high sensitivity and large bandwidth.</p>		
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### Relaxor Ferroelectric Single Crystals for Ultrasound Transducers

This Application is a Continuation in Part of U.S Patent Application Serial No. 08/789,589, filed January 28, 1997, and further claims priority from Provisional Application Serial No. 60/039,611, filed March 12, 1997.

#### FIELD OF THE INVENTION

This invention relates to transducers which employ ferroelectrics and, more particularly, to an electromechanical transducer that is constructed using single crystals of lead zinc niobate - lead titanate or lead magnesium niobate - lead titanate solid-solutions. The compositions exhibit increased phase transition field values, allowing increased transducer driving voltages, decreased fabrication degradation and high electromechanical couplings,  $> 85\%$  and up to a maximum of  $94\%$ .

#### BACKGROUND OF THE INVENTION

##### Piezoelectric Transducers:

Piezoelectric ceramics are currently the material of choice for ultrasonic transducer applications offering relatively high coupling ( $k_{ij}$ ), a wide range of dielectric constants ( $K$ ), and low dielectric loss. These merits translate into transducer performance in the form of relatively high sensitivity, broad bandwidth, impedance matching and minimal thermal heating.

$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) ceramics have been a mainstay for high performance transducer applications. Compositionally, PZT ceramics lie near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases. MPB compositions have anomalously high dielectric and piezoelectric properties as a result of enhanced polarizability arising from coupling between two equivalent energy states, i.e. the tetragonal and rhombohedral phases, allowing optimum domain reorientation during the poling process. Further modifications, using acceptor and donor dopants, give a wide range of piezoelectric compositions.

Alternative MPB systems can be found in relaxor-based ferroelectrics and their solid solutions with  $\text{PbTiO}_3$  (PT). Lead based relaxor materials are complex perovskites with the general formula  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ , ( $\text{B}_1 = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Sc}^{3+} \dots$ ,  $\text{B}_2 = \text{Nb}^{5+}, \text{Ta}^{5+}, \text{W}^{6+} \dots$ ). Characteristic of relaxors is a broad and frequency dispersive dielectric maxima. Some relaxor-PT compositions such as modified  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  -  $\text{PbTiO}_3$  (PSN-PT) seem to possess superior dielectric and piezoelectric properties compared to that of PZT ceramics. However, if analyzed with respect to the ferroelectric

transition temperature  $T_c$  (the temperature at which the material transforms from the prototypical non-ferroelectric to ferroelectric phase being associated with a spontaneous polarization and large dielectric anomaly), no one type of ceramic offers significant advantages in overall transducer performance.

Enhanced piezoelectric activity of MPB-based ceramics by compositionally adjusting the Curie temperature ( $T_c$ ) downward relative to room temperature, comes with the expense of more temperature dependent properties and less polarization stability, i.e. aging and loss of piezoelectric activity.

Though relaxor-PT ceramics do not offer enhanced dielectric and piezoelectric properties comparable to PZT ceramics of similar  $T_c$ 's, it is the single crystal form of relaxor-PT ceramics that exhibits ultrahigh piezoelectric properties not currently available with piezoelectric MPB ceramics. This key distinction was first realized by Yonezawa et al. (Journal of Japanese Society of Powder Metallurgy, Vol 16, pp 253-258, 1969) and later by Kuwata et al. (Ferroelectrics, Vol 37, pp 579-582, 1981) for MPB compositions of  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  -  $\text{PbTiO}_3$  (PZN-PT) systems with  $k_{33}$  values ranging 80 to 90%, followed by crystal growth and evaluation of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  -  $\text{PbTiO}_3$  (PMN-PT).

Although high coupling and piezoelectric properties of the PZN-PT system, first reported in 1969 and later in the PMN-PT system (1989), have been known for several years, their potential for high performance biomedical ultrasound transducers and related devices has only been recognized recently. Serious efforts on the development of  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ -PT crystals for high performance transducers is disclosed in US Patents 5,402,791 and 5,295,487 to Saitoh et al.. Therein are disclosed relaxor based ferroelectric single crystals of lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) solid solutions, where  $0.05 \leq x \leq 0.2$  and  $0.05 \leq y \leq 0.2$ , respectively. It should be noted that the range  $0.05 \leq y \leq 0.2$  for  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  solid solutions described by Saitoh et al. includes the non piezoelectric relaxor (microdomain) region ( $0.05 \leq y < 0.15$ ) at room temperature. For  $0.15 \leq y < 0.20$ , according to this invention, crystals of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  solid solutions exhibit longitudinal coupling  $< 80\%$ , only comparable to MPB ceramics.

When optimum crystallographic cuts, in this case pseudocubic  $\langle 001 \rangle$ , are utilized for rhombohedral crystals, an electric field induced phase transformation from rhombohedral to tetragonal phase can occur under dc bias, because the polar axis in the rhombohedral phase is  $\langle 111 \rangle$ . The phase transition field is strongly dependent upon composition, i. e., the closer to MPB, the lower the transition electric field level because two crystallographic states (rhombohedral and tetragonal) energetically become closer to each other and finally coexist at room temperature when the composition lies on a MPB ( $0.09 \leq x \leq 1.0$  and  $0.35 \leq y \leq 0.40$ , for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  and

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ , respectively).

The rhombohedral-tetragonal phase transition results in discontinuous changes in piezoelectric properties and dimensions. This dimensional change can affect transducer performance during fabrication processes, such as mechanical clamping during poling. Transducer poling normally includes field cooling (cooling under dc-bias from the temperatures above  $T_c$ ).

Figure 3 shows a plot of dielectric constant vs. temperature for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$ , exhibiting transitions from rhombohedral to tetragonal ( $100^\circ\text{C}$ ) and from tetragonal to cubic ( $160^\circ\text{C}$ ). Apart from composition, the phase transition field decreases with increasing temperature. Therefore, increasing temperature under dc bias causes the rhombohedral phase to readily transform into the tetragonal phase.

It should be noted that transducers are attached to multiple quarter wave length matching layers and/or take the form of a low impedance composite comprised of piezoelectric elements with intermediate passive polymer layers, in order to couple acoustic energy and decouple lateral modes. Therefore, successive cooling under bias will cause the crystals to transform back to a rhombohedral phase after the passive polymer becomes significantly rigid at low temperature, resulting in elastically clamped crystals, leading to internal stresses and mechanical failure. Also, stability of rhombohedral phase becomes an issue as the transducer is driven at increased frequencies. To increase driving frequency and thereby obtain enhanced sensitivity, the transducer must be thinner, resulting in an increased electric field at a same driving voltage. Therefore, to avoid a phase transformation with a  $\langle 001 \rangle$  rhombohedral crystal, the driving voltage must be limited. To apply higher voltages for pulse generation, the composition of a rhombohedral crystal should be located appropriately away from the MPB.

In summary, the problems exhibited by compositions of relaxor based single crystals are:

1) Lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) is not piezoelectric at room temperature when  $0.05 \leq y < 0.15$  and does not exhibit piezoelectric properties superior to conventional MPB ceramics when  $0.15 \leq y \leq 0.20$ .

2) For compositions close to MPB for rhombohedral lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ), and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ), where  $0.05 \leq x \leq 0.09$  and  $0.33 < y < 0.40$ , the rhombohedral-tetragonal phase transformation occurs at relatively low fields.

Piezoelectric Actuators:

Electromechanical actuators constructed from piezoelectric or electrostrictive ceramics are used in applications requiring high generative force, high frequency operation, accurate displacement, quick response time, or small device sizes. However, low field induced strain and poor reliability limit the usage of such ceramics for actuator applications.

Electric field induced strain is the most important parameter for actuators. This is demonstrated by the strain energy density which is a measure of the energy per unit mass an actuator can deliver,

$$e_{\max} = 1/\rho \cdot 1/4 \cdot (1/2 \cdot E(\epsilon_{\max})^2)$$

where:  $e_{\max}$  is the strain energy density  $E$  is the actuator's elastic modulus,  $\epsilon_{\max}$  is the maximum field induced strain, and  $\rho$  is the actuator's density. In designing an actuator, the maximum strain energy density should be as high as possible. In electroactive ceramics, density and elastic modulus vary little from material to material. Therefore, level of strain and maximum strain achievable with a reasonable electric field ( $< 50\text{kV/cm}$ ) dominates the energy density parameter.

Strain for a given electric field is determined from a material's piezoelectric coefficient ( $d_{33}$ ). Soft lead-zirconate-titanates (PZT's) and perovskite relaxor-PT( $\text{Pb}((\text{B}_1, \text{B}_2)\text{O}_3)\text{-PbTiO}_3$ , (where  $\text{B}_1 = \text{Mg}^{+2}, \text{Zn}^{+2}, \text{Ni}^{+2}, \text{Sc}^{+3}, \dots$  and  $\text{B}_2 = \text{Nb}^{+5}, \text{Ta}^{+5}, \text{W}^{+6}, \dots$ ) based morphotropic phase boundary (MPB) ceramics offer piezoelectric coefficients  $\sim 600$  to  $700$  pC/N. However the best available actuators offer a maximum strain of not more than  $0.15\%$ . This limitation originates from the material's breakdown strength and polarization saturation.

Soft PZT's and relaxor- $\text{PbTiO}_3$  based ceramics are compositionally engineered to have morphotropic phase boundary (MPB) composition and further engineered to have a decreased paraelectric-ferroelectric transition temperature ( $T_c$ ), resulting in high piezoelectric coefficients. However, this increased piezoelectric activity comes with the expense of large hysteresis, ascribed to electric field induced domain motion. This results in poor positioning accuracy and large heat generation. Heat generation combined with decreased temperature usage range, also results in poor temperature stability of piezoelectric properties. This limits the driving frequency, prohibiting the usage of these high piezoelectric coefficient ceramics for high frequency driving applications.

Strain can be hysteresis minimized with hard piezoelectric ceramics, which exhibit decreased piezoelectric coefficient ( $d_{33}$ ). A hard piezoelectric, such as PZT-4, exhibits piezoelectric coefficients of  $\sim 200$  to  $300$  pC/N.

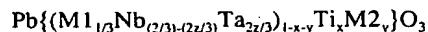
Another category of ceramic materials used in commercial actuators is electrostrictors. Electrostriction strain is proportional to the square of an applied electric field. A few materials such as lead magnesium niobate (PMN) or lead magnesium niobate-lead titanate (PMN-PT) solid solution ceramics with low lead titanate (PT) content exhibit a significant strain ( $> 0.1\%$ ) with virtually no hysteresis.

In summary, the problems of commercially available piezoelectric and electrostrictive ceramics are:

- 1) Low total strain ( $\leq 0.15\%$ ).
- 2) Low strain energy density due to low piezoelectric coefficient ( $d_{33} < 700\text{pC/N}$  and electrical breakdown strength.
- 3) Significant hysteresis which leads to substantial heat generation and poor positioning accuracy.

To achieve strains  $> 0.15\%$ , electroactive materials should possess high piezoelectric coefficients ( $d_{33} > 1000\text{pC/N}$ ) and high breakdown strength.

In the main, the prior art electroactive materials described above are based upon multi-crystalline structures. Saitoh et al. in U.S. Patents 5,295,487 and 5,402,791 describe a range of piezoelectric single crystal materials which exhibit large electromechanical coupling coefficients and teach their use as ultrasound transducers. One set of materials taught by Saitoh et al. is based upon single crystals in the form of solid solutions of zinc lead niobate-lead titanate. Another set of single crystals is given by the formula



where M1 represents one of metals Zn, Ni and Mg, and M2 represents one of Pt, Fe, Bi, Rh and Ir, and x, y and z are defined as  $0.05 \leq x \leq 0.2$ ,  $0.00001 \leq y \leq 0.01$  and  $0 \leq z \leq 0.1$ , respectively.

There is no teaching by Saitoh et al. that only a certain subset of their materials will exhibit a high strain factor (it being known to those skilled in the art that high coupling coefficients do not necessarily equate to high strain factors). As will be apparent from the description of the invention below, Applicants have discovered that a subset of the materials of Saitoh et al. exhibit large strains so long as an electric field is applied thereto generally along the 001 crystalline axis.

### SUMMARY OF THE INVENTION

<001> oriented crystals of lead zinc niobate - lead titanate solid solution (0 to 5 mole% lead titanate) have high electromechanical coupling > 85% and exhibit electric field induced phase transitions at electric field levels >  $10 \times E_c$  (where  $E_c$  is the coercive field), resulting in increased transducer driving voltages, decreased fabrication degradation, and high sensitivity/large bandwidth transducer characteristics due to high electromechanical couplings, up to 92%. <001> oriented crystals of lead magnesium niobate - lead titanate solid solution (20 to 50 mole% lead titanate) also exhibit high electromechanical couplings > 85% and up to 94%, and thereby can be formed into transducers which exhibit both high sensitivity and large bandwidth.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1a and 1b show ultrasound transducers, in accordance with the invention, comprising single crystal piezoelectric elements and intervening polymers.

Figs. 2a and 2b show the phase diagrams of lead zinc niobate -lead titanate and lead magnesium niobate-lead titanate solid solutions, respectively.

Fig. 3 shows a dielectric constant vs. temperature curve for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$ , exhibiting transitions from rhombohedral to tetragonal ( $100^\circ\text{C}$ ) and tetragonal to cubic ( $160^\circ\text{C}$ ).

Fig. 4 shows longitudinal couplings as a function of composition and crystal orientation for lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$ .

Fig. 5 shows longitudinal couplings as a function of composition and crystal orientation for lead magnesium niobate - lead titanate  $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$ .

Figs. 6a, 6b, 6c show  $P=f(E)$  curves of <001> oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals for  $x=0$ ,  $x=0.045$ , and  $x=0.08$ , respectively.

Fig. 7 shows  $P=f(E)$  curves for <111> and <001> oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals for  $x=0$ , with applied unipolar electric fields, after poling (applying  $10 \times E_c$  at room temperature).

Fig. 8 shows  $P=f(E)$  curves for <001> oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals for  $x=0$ ,  $x=0.045$ , and  $x=0.08$ , respectively, with unipolar electric field applied after poling (applying  $10 \times E_c$  at room temperature).



Fig. 9 shows strain vs. electric field curves for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals for  $x=0$ ,  $x=0.02$ ,  $x=0.045$ ,  $x=0.06$  and  $x=0.08$ , respectively, with unipolar electric field applied after poling (applying  $10x E_c$  at room temperature).

Fig. 10 shows  $E_c$  and phase transition fields as a function of composition, for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals.

Fig. 11 shows  $E_c$  and phase transition fields as a function of composition for  $\langle 001 \rangle$  oriented lead magnesium niobate - lead titanate  $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3)$  crystals.

Fig. 12 shows a perspective view of an actuator incorporating a single crystalline ferroelectric wherein an electric field is applied along the  $\langle 001 \rangle$  crystallographic axis.

Figs. 13a, 13b shows phase diagrams of lead zinc niobate-lead titanate and lead magnesium niobate-lead titanate solid solutions.

Fig. 14 shows a plot of strain as a function of electric field for  $\langle 001 \rangle$  oriented rhombohedral crystals  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ , ( $x=0.0, 0.045, 0.08$ ) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ , ( $y=0.24$ ).

Fig. 15 shows plots of strain vs. electric field for samples with different crystal orientations.

Fig. 16 shows plots of strain vs. electric field for  $\langle 001 \rangle$  oriented  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.905}\text{Ti}_{0.095}\text{O}_3$  crystal as an example of MPB behavior.

Fig. 17 shows plots of strain as a function of electric field for various  $\langle 001 \rangle$  oriented rhombohedral crystals  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3, (x=0, 0.045, 0.08))$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3, (y=0.24)$ , where hysteresis is low up to the maximum applied electric field.

Fig. 18 shows plots of strain as a function of electric field for various  $\langle 001 \rangle$  oriented rhombohedral crystals  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3, (x=0, 0.045, 0.08))$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3, (y=0.24))$ , where electric field is applied until the samples electrically break down.

Fig. 19 shows representative  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction.

Figs. 20, 21 show plots of low field ( $< 40\text{kV/cm}$ ) strain behavior for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of

deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction, for various values of  $\alpha$ .

Fig. 22 shows plots of high field ( $\cong 100\text{kV/cm}$ ) strain behavior for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction, for various values of  $\alpha$ .

Fig. 23 shows a plot of hysteresis as a function of  $\alpha$  for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction.

Fig. 24 shows a plot of strain hysteresis as a function of  $\alpha$  for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

### Piezoelectric Transducers:

This invention establishes structural property relationships, optimum compositions and crystallographic orientations for single crystals of lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) solid solutions, which obtain ultrahigh electromechanical coupling and avoid induced phase transitions during transducer fabrication and driving. Based on the commonalities inherent to relaxor-PT systems, this invention considers two representative systems of lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ). Though lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) crystals exhibit piezoelectric properties comparable with lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ), more focus is given to the lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) system, owing to its relatively lower PT content for MPB. This allows more uniform crystal growth of such solid solution materials.

The crystals were fabricated as follows. High purity ( $>99.9\%$ ) powders of  $\text{Pb}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{MgCO}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  were used as starting materials. Raw powders were weighed in desired molar ratios with excess  $\text{Pb}_3\text{O}_4$  as a flux. The powder was dry mixed for a desired period of time using a tumbling mill. Mixed powder was loaded into a platinum crucible, which was then placed in an alumina crucible sealed with an alumina lid and alumina cement to minimize  $\text{PbO}$  volatilization. The crucible and powder were then placed in a tube furnace and held at an appropriate soak temperature above the melting temperature, followed by slow cooling. The crucible was then furnace-cooled to room temperature. Hot  $\text{HNO}_3$  was used to separate the crystals from of the rest of the melt.

The crystals of lead zinc niobate - lead titanate and lead magnesium niobate - lead titanate solid solutions can similarly be fabricated using, i.e., the top seeded solution growth method (TSSG), the submerged seeded solution growth method, Kyropoulos method, the hydrothermal method, the Bridgman method, and the solid state growth technique (exaggerated grain growth), in addition to the flux method described above. Other crystal forms can be used. For example, material bodies comprising a textured structure or epitaxially grown films also show superior behavior. Further, the crystals can contain certain amounts of impurities from chemicals and crucibles, i.e. Pt, Ir, Rh, Fe, and Bi.

The piezoelectric properties were measured as follows. For longitudinal coupling ( $k_{33}$ ) determinations, bar shape samples with lengths ranging from 3 mm to 5 mm were used. The piezoelectric coefficient ( $k_{33}$ ) was calculated based on IEEE standards. Individual crystals were oriented along their pseudocubic axes  $\langle 111 \rangle$  and  $\langle 001 \rangle$ , using a Laue back reflection camera. For electrical characterization, samples were prepared by polishing with silicon carbide and alumina polishing powders to achieve flat and parallel surfaces, onto which gold electrodes were sputtered. High-field measurements, including polarization and strain hysteresis, were made using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT), driven by a lock-in amplifier (Stanford Research Systems, Model SR830). Plate shaped samples with thicknesses ranging from 0.2 mm to 0.5 mm were used. The voltage was supplied using a Trek 609C-6 high voltage DC amplifier. Through use of the LVDT sensor, sample strain was measured when a field was applied. Electric fields as high as  $\sim 140$  kV/cm could be applied using an amplified unipolar waveform at 0.2 Hz. During testing the samples were submerged in Fluorinert (FC-40, 3M, St. Paul, MN), an insulating liquid, to prevent arcing.

Piezoelectric single crystals according to the present invention are expressed by formulae 1-4 below:



where:  $x$  is defined as  $0 \leq x < 0.05$ . With these compositions, crystals have a rhombohedral structure and crystals oriented along pseudocubic  $\langle 001 \rangle$  direction exhibit longitudinal couplings  $> 85\%$ . If  $x > 0.05$ ,  $\langle 001 \rangle$  oriented rhombohedral  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  crystals transform into a tetragonal phase at electric fields lower than a  $10\times$  coercive field ( $E_c$ ), limiting transducer driving voltage and increasing fabrication degradation.



where:  $y$  is defined as  $0.20 < y \leq 0.50$ . With these compositions, crystals oriented along the

pseudocubic  $\langle 001 \rangle$  direction exhibit longitudinal coupling  $> 80\%$ . If  $0 \leq y < 0.15$ ,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  crystals are not piezoelectric without a dc-bias at room temperature. If  $0.15 \leq y \leq 0.2$ ,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  crystals exhibits longitudinal couplings lower than  $80\%$ .



where:  $y$  is defined as  $0.20 < y \leq 0.35$ . With these compositions, crystals have rhombohedral structure and crystals oriented along pseudocubic  $\langle 001 \rangle$  direction exhibit longitudinal couplings  $> 80\%$ .



where:  $y$  is defined as  $0.35 \leq y \leq 0.50$ . With these compositions, crystals have MPB or tetragonal structure and crystals oriented along pseudocubic  $\langle 001 \rangle$  direction exhibit longitudinal couplings  $> 85\%$ , comparable to those observed with formula 1.

It is more preferable to use the crystals with the compositions of:



where;  $y$  is defined as  $0.25 \leq y \leq 0.33$ . With these rhombohedral compositions,  $\langle 001 \rangle$  oriented crystals possess longitudinal couplings  $> 85\%$  with a maximum value of  $\sim 94\%$ . However, if  $0.33 < y \leq 0.40$ , the resulting composition is close to the MPB or lies on the MPB, resulting in  $\langle 001 \rangle$  oriented rhombohedral  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  crystals which transform into a tetragonal phase at significantly lower electric fields, e.g.,  $< 10 \times$  coercive field ( $E_c$ ).

Fig. 1a shows an exploded view of 2-2 composite ultrasound transducer 100, comprising plural single crystal piezoelectric elements 102, encompassing polymer layers 104 and electrodes 106 and 108. Fig. 1b shows an exploded view of 1-3 composite ultrasound transducer 110, comprising plural single crystal piezoelectric elements 112, encompassing polymer layers 114 and electrodes 116 and 118.

Ultrasound transducer 100 is manufactured by the following method. Transducer fabrication from an as-grown single crystal began with orientation using a Laue back reflection camera. Once a reference face parallel to the  $(001)$  plane was polished into the crystal, the crystal was sliced parallel to the reference face to approximately 1 mm. This slice was then polished flat and gold sputtered on both sides. An electric field, as high as  $10 \times$  the coercive field ( $E_c$ ), was applied to pole the slice. Kerfs were cut into the material parallel to  $\langle 100 \rangle$ , using standard dicing technology, such as a Kulicke and Soffa 782 wafer dicing saw. The cut spaces were then filled with polymer, such as Hysol

2038/3404 epoxy. The composite was polished again down to a determined thickness and gold was sputtered on both sides. To make sure poling was complete, electric fields as high as  $10 \times E_c$  were then applied at temperatures above the polymer softening temperature (in this case  $\sim 60^\circ\text{C}$ ). The composite was then cooled, under dc-bias, to room temperature.

Figs. 2a and 2b show phase diagrams of lead zinc niobate - lead titanate and lead magnesium niobate-lead titanate solid solutions, respectively. The dots reflect the crystal compositions tested in the process of making this invention, and the solid dots represent the compositions that fall within the claimed ranges of this invention.

Fig. 3 shows variations of dielectric constant vs. temperature for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$ , exhibiting transitions from rhombohedral to tetragonal ( $100^\circ\text{C}$ ) and tetragonal to cubic ( $160^\circ\text{C}$ ). Increased temperature, together with dc bias, cause the rhombohedral phase to readily transform to the tetragonal phase. This occurs for all  $\langle 001 \rangle$  oriented rhombohedral crystals of lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) solid solutions, where  $0 \leq x < 0.09$  and  $0.15 \leq y \leq 0.35$ , respectively.

Stability of the rhombohedral phase during poling becomes an issue for  $0.05 \leq x < 0.09$  and  $0.33 \leq y \leq 0.35$ , as transition fields are less than  $10 \times E_c$  at room temperature (where the rhombohedral-tetragonal transition occurs at much lower field intensities with increased temperature). Also, rhombohedral phase stability issues limit transducer driving voltage, especially at high driving frequencies. To increase the driving frequency for enhanced sensitivity, the transducer must be thinner, resulting in an increased electric field at the same driving voltage. Therefore, use of a  $\langle 001 \rangle$  rhombohedral crystal limits the transducer driving voltage, unless composition of the rhombohedral crystal is adjusted to be appropriately distant from the MPB.

Table 1 presents dielectric and piezoelectric properties, calculated based on IEEE standards, as a function of composition and crystal orientation. High longitudinal couplings ( $k_{33} > 85\%$ ) can be observed with crystals oriented along the pseudocubic  $\langle 001 \rangle$  direction.  $\langle 111 \rangle$  oriented rhombohedral crystals of lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) and lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ), where  $0 \leq x < 0.9$  and  $0.2 < y < 0.35$ , exhibited inferior couplings  $< 40\%$ . If  $0.15 \leq y \leq 0.2$ , lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) solid solutions possess longitudinal coupling  $< 80\%$ , only comparable to the conventional MPB ceramics such as PZT.

Table 1: Piezoelectric Properties of various PZN-PT and PMN-PT crystals (longitudinal mode)

Composition	Crystal Structure	Orient.	coupling	$s_{33}^E$ ( $10^{-12} \text{m}^2/\text{N}$ )	$K_3$ <sup>1</sup>	loss	$d_{33}$ (pC/N)
PZN	Rhom <sup>1</sup>	111	0.38	7.4	900	0.012	83
		001	0.85	48	3600	0.008	1100
PZN-2%PT	Rhom	111	0.38	7.7	900	0.004	90
		001	0.87	74	3800	0.010	1550
PZN-4.5%PT	Rhom	111	0.35	9.0	1500	0.004	110
		001	0.92	102	4000	0.004	2000
PZN-6%PT	Rhom	111	0.33	7.3	710	0.004	74
		001	0.93	130	4500	0.012	2400
PZN-8%PT	Rhom	111	0.39	7.4	2150	0.012	82
		001	0.94	130	4200	0.012	2400
PZN-9.5%PT	MPB <sup>2</sup>	111	0.64	10.4	4300	0.007	600
		001	0.89	77	1600	0.004	1600
PZN-12%PT	Tetra <sup>3</sup>	001	0.86		900	0.004	500
PMN-24%PT	Rhom	001	0.84	54	3700	0.009	900
PMN-33%PT	Rhom	001	0.94	79	4500	0.012	1700
PMN-35%PT	MPB	001	0.92	67	3100	0.014	1240
PMN-40%PT	Tetra	001	0.85		1000	0.005	

<sup>1</sup> rhombohedral.<sup>2</sup> morphotropic phase boundary - coexistence of both rhombohedral and tetragonal phases.<sup>3</sup> tetragonal.

From Table 1, it can be concluded that compositions of lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) crystals must be  $0.20 < y \leq 0.50$ , in order to obtain ultrahigh couplings  $> 80\%$ . More particularly, compositions of lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) crystals should preferably be  $0.25 \leq y \leq 0.50$  to have longitudinal couplings higher than  $85\%$ , comparable to lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ). High couplings  $> 85\%$  with low dielectric constants ( $< 1000$ ) for tetragonal lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ) crystals  $0.38 < y \leq 0.50$  illustrate significant usefulness for single element transducers, as this type of transducer requires high electromechanical coupling, with a low dielectric constant for electrical impedance matching.

Fig. 4 shows plots of longitudinal coupling as a function of composition and crystal orientation, for lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ). It can be seen that closeness to the MPB is not essential to obtain ultrahigh coupling, if rhombohedral crystals are oriented along the  $\langle 001 \rangle$  axis. Solid dots indicate coupling values as a function of compositions that are within the scope of the invention.

Fig. 5 shows plots of longitudinal coupling as a function of composition and crystal orientation for lead magnesium niobate - lead titanate ( $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$ ). Couplings  $> 80\%$  can

be observed for the compositions  $0.2 < y \leq 0.5$ . Solid dots indicate coupling values as a function of compositions that are within the scope of the invention..

Figs. 6a, 6b, 6c show  $P=f(E)$  curves of  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) crystals for  $x=0$ ,  $x=0.045$ , and  $x=0.08$ , respectively. All  $\langle 001 \rangle$  oriented crystals exhibited ferroelectric hysteresis similar to those observed with single domain switching, implying a stable domain configuration. Coercive fields ( $E_c$ ), where orientation of ferroelectric domains occurs by application of an electric field, were found to be almost the same ( $\sim 3\text{kV/cm}$ ) for all  $\langle 001 \rangle$  oriented rhombohedral crystals. The larger  $P_s$  ( $35 \mu\text{C/cm}^2$ ) and hump in  $P=f(E)$  curve observed with  $\langle 001 \rangle$  oriented  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$  crystals are related to the rhombohedral to tetragonal phase transition.

Fig. 7 shows  $P=f(E)$  curves for  $\langle 111 \rangle$  and  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) crystals for  $x=0$ , with a unipolar electric field applied, after poling (applying  $10 \times E_c$  at room temperature). All  $\langle 001 \rangle$  oriented rhombohedral crystals exhibited hysteresis-free behavior, resulting from a stable domain configuration. However, domain instability with  $\langle 111 \rangle$  oriented rhombohedral crystals resulted in hysteresis in  $P=f(E)$  curves and inferior piezoelectric properties, as presented in Table 1.

Fig. 8 shows  $P=f(E)$  curves for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) crystals for  $x=0$ ,  $x=0.045$ , and  $x=0.08$ , respectively, with an applied unipolar electric field, after poling (applying  $10 \times E_c$  at room temperature). Each crystal exhibited a discontinuous increase in polarization at the electric fields, the amount of which was inversely proportional to  $x$ . This discontinuous increase in  $P=f(E)$  curves and resultant hysteresis are caused by an electric field-induced phase transformation, i.e., rhombohedral to tetragonal transition for  $\langle 001 \rangle$  oriented rhombohedral crystals.

Fig. 9 shows strain vs. electric field curves for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) crystals for  $x=0$ ,  $x=0.02$ ,  $x=0.045$ ,  $x=0.06$  and  $x=0.08$ , respectively, with an applied unipolar electric field, after poling (applying  $10 \times E_c$  at room temperature). Associated with the phase transition, strain increased abruptly and a large hysteresis can be observed. This large strain during the induced phase transition, resulted in an increased fabrication failure rate and limited the transducer driving voltage.

Fig. 10 shows  $E_c$  and phase transition fields as a function of composition, for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ) crystals.  $E_c$  ( $\sim 3\text{kV/cm}$ ) does not vary significantly as a function of composition, but the transition field is strongly dependent upon composition. Electric fields  $> 10 \times E_c$  can be applied without causing a phase transformation at room

temperature for  $\langle 001 \rangle$  oriented lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$  crystals, when compositions are  $0 \leq x < 0.05$ . Crystals with compositions  $0 \leq x < 0.05$  have a  $T_c$  lower than those  $x \geq 0.05$ , possibly resulting in more temperature dependent properties, and less polarization stability. However, as shown in the phase diagram of lead zinc niobate - lead titanate  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3)$ , Fig. 2),  $T_c$  increases with increased  $x$ , whereas the rhombohedral - tetragonal transition temperature decreases, the latter being more critical during fabrication and driving. Also, transducer temperature can be maintained constant by using PTCR (positive temperature coefficient resistor) ceramics such as doped  $\text{BaTiO}_3$ .

Fig. 11 shows  $E_c$  and phase transition fields as a function of composition for  $\langle 001 \rangle$  oriented lead magnesium niobate - lead titanate  $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3)$  crystals.  $E_c$  ( $\sim 3\text{kV/cm}$ ) does not vary significantly as a function of composition, but the transition field is strongly dependent upon composition. Electric fields  $> 10 \times E_c$  can be applied without causing a phase transformation at room temperature for  $\langle 001 \rangle$  oriented lead magnesium niobate - lead titanate  $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3)$  crystals, when compositions are  $y \leq 0.33$ .

#### Experimental

Transducers using  $\langle 001 \rangle$  oriented rhombohedral  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals and rhombohedral  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$  crystals were manufactured as shown in Fig. 1. As-grown single crystals were oriented using a Laue back reflection camera. Once a reference face parallel to the  $(001)$  plane was polished into the crystal, the crystals were sliced parallel to the reference face to approximately 1 mm. The slice was then polished flat, and gold was sputtered on both sides. Electric fields as high as  $10 \times E_c$  were applied to pole the disk. Kerfs were cut into the material, parallel to  $\langle 100 \rangle$ , using standard dicing technology such as a Kulicke and Soffa 782 wafer dicing saw. The cut spaces were then filled with polymers such as Hysol 2038/3404 epoxy. The composite was polished again down to a determined thickness and gold was sputtered on both sides. To make sure poling was complete, electric fields as high as  $\sim 10 \times E_c$  were then applied at temperatures above the polymer softening temperature (in this case  $\sim 60^\circ\text{C}$ ). The composite was cooled under dc-bias, down to room temperature.

Table 2 presents longitudinal coupling values ( $k_{33}$ ) for a single element transducer and couplings measured from a  $2 \times 2$  composite ( $k_{\text{bar}}$ ). Mechanical clamping by tall and narrow element shape (lateral clamping) and by the rigid polymer results in decreased values of  $k_{\text{bar}}$ . However, further decreases in  $k_{\text{bar}}$  can be found in example 2 below, with increased mechanical failure resulting from the phase transformation during poling. It should be noted that, even though a single longitudinal bar having a composition closer to the MPB exhibits higher couplings, subsequent couplings of composites are higher for the compositions that are positioned away from MPB.



Table 2.

	Composition	orien- tation	$k_{33}$ for single element	$k_{bar}$ for 2-2 composite	survived transducers
example 1	$Pb(Zn_{1/3}Nb_{2/3})_{0.955}Ti_{0.045}O_3$	<001>	92%	89%	90%
example 2	$Pb(Zn_{1/3}Nb_{2/3})_{0.92}Ti_{0.08}O_3$	<001>	94%	70%	75%

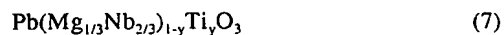
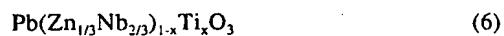
### Piezoelectric Actuators

It has been found that certain single crystal ferroelectrics will evidence very high strain values if their constituents restrict their crystalline form to the rhombohedral structure and an electric field is applied thereacross so as to be in general alignment with the <001> crystallographic axis. Such ferroelectrics exhibit very low levels of hysteresis and thus may be driven at relatively high frequencies without overheating. The materials comprising the invention are preferably in solid solution form.

Single crystalline ferroelectrics, which exhibit large strain and low hysteresis and are usable with actuators incorporating the invention, are solid solutions of lead zinc niobate-lead titanate or lead magnesium niobate-lead titanate, which possesses a large piezoelectric coefficient ( $d_{33}$  - 1000 pC/N to 2500 pC/N), and a maximum strain > 1.2%.

In Fig. 12, an actuator 10 incorporating the invention comprises a ferroelectric body 12 that is bounded by conductive electrodes 14 and 16. Body 12 comprises a single crystal solid solution of the chosen ferroelectric composition and the crystal axes of the crystal are generally aligned as shown by coordinates 20. When a voltage V is applied across electrodes 14 and 16, ferroelectric body 12 is poled as shown by arrow 24.

A ferroelectric single crystal according to the present invention is described by formulae 1 and 2 below:



where: x and y are defined as  $0 \leq x < 0.10$ , and  $0 \leq y < 0.40$ , respectively. If  $x > 0.1$  and  $y > 0.4$ , the single crystals have a tetragonal structure with piezoelectric coefficients as low as 500 pC/N.

A more preferred range of limits for x and y are  $0 \leq x < 0.09$ , and  $0 \leq y < 0.35$ , resulting in rhombohedral crystalline structure. In the range of  $0.09 \leq x \leq 0.1$  and  $0.35 \leq y \leq 0.4$ , crystals lie on

morphotropic phase boundaries (MPB), with coexisting rhombohedral and tetragonal phases. In spite of observed strain as high as 1% and large low field piezoelectric coefficients ( $d_{33} \approx 1500$  pC/N) for MPB crystals, large hysteresis associated with domain motion and phase transition is observed when strain is plotted versus applied electric field for such MPB crystals. Thus while such compositions are usable and exhibit large strain values, their range of applications is not as wide as materials in the more preferred ranges of  $x$  and  $y$ .

Piezoelectric single crystals of formulae 6 and 7 should be oriented and poled generally along the pseudocubic  $\langle 001 \rangle$  direction to obtain a large strain value with little or no hysteresis effects.

### EXPERIMENTAL

The piezoelectric coefficients ( $d_{33}$ ) of lead zinc niobate-lead titanate and lead magnesium niobate-lead titanate solid solution single crystals were measured using direct observation of strain as a function of electric field as well as calculations based on IRE standards.

The crystals were fabricated as follows: High purity ( $>99.9\%$ ) powders of  $Pb_3O_4$ ,  $ZnO$ ,  $MgCO_3$ ,  $Nb_2O_5$  and  $TiO_2$  were used as starting material. Raw powders were weighed with desired molar ratio with excess  $Pb_3O_4$  as a flux. The powder was dry mixed for a desired period of time using a tumbling mill. Mixed powder was loaded into a platinum crucible, which was then placed in an alumina crucible sealed with an alumina lid and alumina cement to minimize  $PbO$  volatilization. The crucible and powder were then placed in a tube furnace and held at an appropriate soak temperature above melting temperature, followed by slow cooling. The crucible was then furnace-cooled to room temperature. Hot  $HNO_3$  was used to separate the crystals out of the rest of the melt.

Crystals of lead zinc niobate - lead titanate and lead magnesium niobate - lead titanate solid solutions can similarly be fabricated using a top seeded solution growth method (TSSG), a submerged seeded solution growth method, Kyropoulos method, the hydrothermal method, solid state reaction via exaggerated grain growth and the Bridgman method, in addition to the flux method described above. Also, single crystals or pseudocrystals that consist of multiple single crystals of lead zinc niobate-lead titanate and lead magnesium niobate-lead titanate solid solutions can be fabricated using textured growth or epitaxial growth, that is, the growth of crystals of one material on the crystal surface of another material, such that the crystalline substrates of both materials have the same structural orientation.

The piezoelectric properties were measured as follows: Individual crystals were oriented along their pseudocubic  $\langle 111 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 001 \rangle$  directions using a Laue back reflection camera. For electrical characterization, samples were prepared by polishing with silicon carbide and

alumina polishing powders to achieve flat and parallel surfaces onto which gold electrodes were sputtered.

High-field measurements included polarization and strain hysteresis using a linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR830). Plate shape samples with the thickness ranged from 0.2 mm to 0.5 mm were used. The voltage was supplied using a Trek 609C-6 high voltage DC amplifier. Through the LVDT sensor the strain of the samples was measured with the application of applied fields. Electric fields as high as ~140 kV/cm were applied using an amplified unipolar wave form at 0.2 Hz.

During testing the samples were submerged in Fluorinert (FC-40, 3M, St. Paul, MN), an insulating liquid, to prevent arcing. For piezoelectric coefficient ( $d_{33}$ ) determination, bar shape samples with the lengths which ranged from 3 mm to 5 mm were used. Piezoelectric coefficient ( $d_{33}$ ) was calculated based on IRE standards.

Figs. 13a and 13b show phase diagrams of lead zinc niobate - lead titanate and lead magnesium niobate-lead titanate solid solutions, respectively. The solid dots are the crystal compositions which were tested during the development of the invention.

Table 3 presents low field dielectric and piezoelectric properties, calculated based on IRE standards, as a function of composition and crystal orientation. High piezoelectric coefficient ( $d_{33} > 1000$  pC/N) crystals had a rhombohedral structure or MPB composition and orientation along pseudocubic  $\langle 001 \rangle$  direction. Piezoelectric coefficients as high as 2200 were measured for (001) oriented rhombohedral crystals of  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$ .

Table 3. Low Field Piezoelectric Properties of Various PZN-PT and PMN-PT Crystals.

Composition	Crystal Structure	Orient.	coupling	$s_{33}^E$ ( $10^{-12} \text{ m}^2/\text{N}$ )	$K_3$ <sup>1</sup>	loss	$d_{33}$ (pC/N)
PZN	Rhom <sup>1</sup>	111	0.38	7.4	900	0.012	83
		001	0.85	48	3600	0.008	<b>1100</b>
PZN-4.5%PT	Rhom	111	0.35	9.0	1500	0.004	110
		001	0.91	102	4000	0.004	<b>2000</b>
PZN-8%PT	Rhom	111	0.39	7.4	2150	0.012	82
		001	0.94	130	4200	0.012	<b>2200</b>
PZN-9.5%PT	MPB <sup>2</sup>	111	0.64	10.4	4300	0.007	600
		001	0.89	77	1600	0.004	<b>1600</b>
PZN-12%PT	Tetra <sup>3</sup>	001	0.86		900	0.004	500
PMN-24%PT	Rhom	001			3700	0.009	900
PMN-33%PT	Rhom	001	0.94	79	4500	0.012	<b>1700</b>
PMN-35%PT	MPB	001	0.92	67	3100	0.014	<b>1240</b>

<sup>1</sup> rhombohedral.<sup>2</sup> morphotropic phase boundary - coexistence of both rhombohedral and tetragonal phases.<sup>3</sup> tetragonal.

Fig. 14 shows a plot of strain as a function of electric field for various <001> oriented rhombohedral crystals  $(\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  ( $x=0, 0.045, 0.08$ ) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  ( $y=0.24$ )). Piezoelectric coefficients ( $d_{33}$ ) directly calculated from the slope of strain vs. electric field curves confirmed the values of piezoelectric coefficients presented in Table 3. A  $d_{33}$  value >2500 pC/N was directly measured from the slope of the strain versus electric field curve for a <001> oriented  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$  crystal.

Low hysteresis behaviors are apparent from the plots of Fig. 14. That behavior can be ascribed to a stable domain configuration. Strain behavior of piezoelectric ceramics (PZT-5H) with the largest piezoelectric coefficient ( $d_{33} \sim 750 \text{pC/N}$ ) is compared with those of single crystals in the Fig.

Fig. 15 shows examples of strain vs. electric field for samples with different crystal orientations.  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.92}\text{Ti}_{0.08}\text{O}_3$  crystal oriented along the pseudocubic  $\langle 111 \rangle$  and  $\langle 001 \rangle$  directions and a  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystal oriented along the pseudocubic  $\langle 110 \rangle$  direction were chosen as examples. E-field induced strain deviated from linearity and exhibited large hysteresis due to domain motion for crystals oriented along  $\langle 111 \rangle$  and  $\langle 110 \rangle$  directions. It was concluded that pseudocubic  $\langle 001 \rangle$  was the direction resulting in a hysteresis strain.

Fig. 16 shows the strain vs. electric field curve for  $\langle 001 \rangle$  oriented  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.905}\text{Ti}_{0.095}\text{O}_3$  crystal as an example of MPB behavior. Strain as high as 1 % was observed, with large hysteresis due to the electric field induced domain motion. It is believed that the rhombohedral-tetragonal phase transition is also related to this hysteresis. It was concluded that the crystal must be rhombohedral to have low hysteresis strain behavior.

Fig. 17 shows the strain as a function of electric field for various  $\langle 001 \rangle$  oriented rhombohedral crystals ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  ( $x=0, 0.045, 0.08$ ) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  ( $y=0.24$ )), where hysteresis is low, up to the maximum applied electric field. Low hysteresis strain up to 0.55% was observed. Strains of various piezoelectric ceramics such as soft PZT (PZT-5H), hard PZT (PZT-8) and of electrostrictive ceramics are compared in the Fig.

Fig. 18 shows the strain as a function of electric field for various  $\langle 001 \rangle$  oriented rhombohedral crystals ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$  ( $x=0, 0.045, 0.08$ ) and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-y}\text{Ti}_y\text{O}_3$  ( $y=0.24$ )), where electric field is applied until the samples electrically break down. Samples undergo an electric field induced rhombohedral-tetragonal transition, resulting in hysteresis. Strains as high as 0.8% were observed for all tested crystal samples.  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystal did not experience electric break down within the voltage limit of apparatus, resulting in strain  $> 1.2\%$ .

Figs. 19-22 are plots which demonstrate that strain values of materials having the preferred composition ratios vary when the electric field is not aligned with the  $\langle 001 \rangle$  crystallographic axis. However it is to be noted that so long as the electric field vector is within  $\pm 20^\circ$ , that acceptable strain values and hysteresis levels are obtained. More specifically, Fig. 8 shows representative  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction. This Fig. illustrates the deviation of the crystal orientation from an electric field applied along the  $\langle 001 \rangle$  axis.

Figs. 20, 21 show plots of low field ( $<40\text{ kV/cm}$ ) strain behavior for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction, for various values of  $\alpha$ . It is to be noted that when  $\alpha$  exceeds  $20^\circ$ , the level of hysteresis increases substantially.

Fig. 22 shows plots of high field ( $\cong 100\text{ kV/cm}$ ) strain behavior for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction, where  $\alpha$  is the degree of deviation toward  $\langle 111 \rangle$  from the exact  $\langle 001 \rangle$  direction, for various values of  $\alpha$ . It is to be noted that when  $\alpha$  exceeds  $20^\circ$ , the achievable strain value decreases markedly. Further, increased breakdown strength allowed a  $\langle 001 \rangle$  crystal to exhibit strain as high as 1.5%.

Fig. 23 shows a plot of hysteresis as a function of  $\alpha$  for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction. Hysteresis values were calculated from polarization vs. unipolar electric field when the maximum applied field was  $20\text{ kV/cm}$  for all crystals. Fig. 23 indicates that hysteresis caused by domain motion increases with increased value of  $\alpha$ , resulting in more heat generation. The increased hysteresis also implies that strain values are not reproducible at the same electric field, a characteristic which is to be avoided for positioner applications.

Fig. 24 shows a plot relative values of strain hysteresis as a function of  $\alpha$  for  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.955}\text{Ti}_{0.045}\text{O}_3$  crystals oriented along  $\langle 001 \rangle + \alpha$  direction. Relative values of strain hysteresis were calculated from the equation  $(S_d - S_i)/S_i$ , where  $S_d$  and  $S_i$  are strain values at  $5\text{ kV/cm}$  with increasing and decreasing the electric field, respectively, and when the maximum applied electric field was  $20\text{ kV/cm}$ . Ideally, these values should be zero, resulting in no hysteresis of strain and perfect positional reproducibility. From Fig. 13, it is seen that strain hysteresis increases abruptly at about  $\alpha = 20^\circ$ .

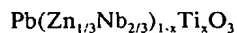
In summary, single crystals of the preferred ferroelectric compositions were found to have a piezoelectric coefficient ( $d_{33}$ ) as high as  $2500\text{ pC/N}$ , maximum electric field induced strains of 1.3% and very low strain-electric field hysteresis. (So long as the applied electric field was applied generally along the  $\langle 001 \rangle$  crystallographic axis.)

It should be understood that the foregoing description is only illustrative of the invention. Various alternatives and modifications can be devised by those skilled in the art without departing from the invention. For instance, other rhombohedral relaxor -  $\text{PLbTiO}_3$  crystals will likely exhibit high strain so long as their  $\langle 001 \rangle$  crystallographic axes are oriented  $\pm 20^\circ$  from a common directional orientation. Also, while the invention has been described in the context of a single crystal actuator configuration, pseudocrystals that consist of multiple single crystals can be utilized so long as their  $\langle 001 \rangle$  crystallographic axes are oriented  $\pm 20^\circ$  from a common directional orientation.

These multiple single crystals can be fabricated using textured growth or epitaxial growth, that is, the growth of crystals of one material on the crystal surface of another material, such that the crystalline substrates of both materials have the same structural orientation. Accordingly, the present invention is intended to embrace all such alternatives, modifications and variances which fall within the scope of the appended claims.

## CLAIMS

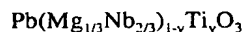
1. A transducer comprising single crystals of a lead zinc niobate-lead titanate solid solution, wherein said single crystals of lead zinc niobate-lead titanate solid solution have a composition represented by the formulae:



where: x is within the following limits:  $0 \leq x < 0.05$ .

2. The transducer as recited in claim 1, wherein said single crystals are oriented along their respective pseudocubic  $\langle 001 \rangle$  direction.

3. A transducer comprising single crystals of lead magnesium niobate-lead titanate, wherein said single crystals of lead magnesium niobate-lead titanate solid solution have composition represented by the formulae:



where y is within the following limits:  $0.20 < y \leq 0.50$ .

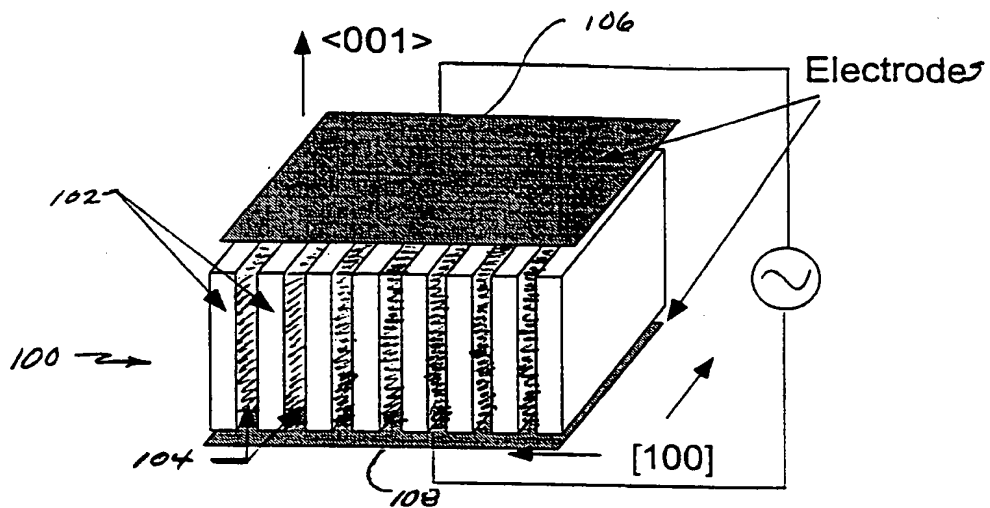
4. The transducer as recited in claim 3, wherein y is within the following limits:  $0.20 < y \leq 0.35$ .

5. The transducer as recited in claim 3, wherein y is within the following limits:  $0.35 < y \leq 0.50$ .

6. The transducer as recited in claim 3, wherein y is within the following limits:  $0.25 < y \leq 0.33$ .

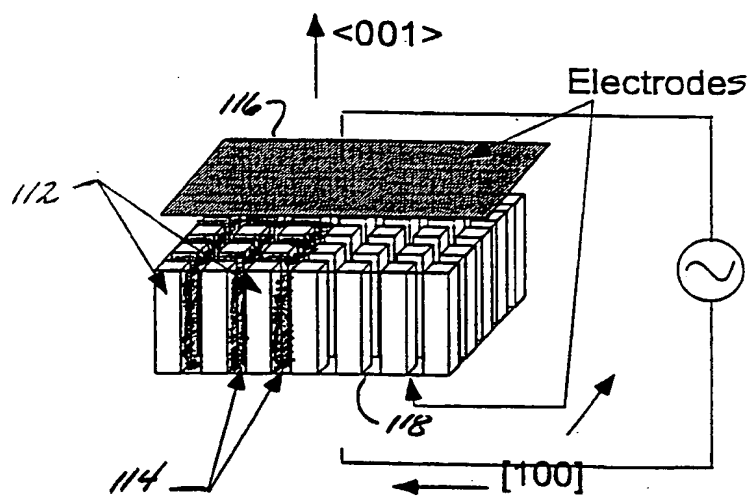
7. The transducer as recited in claim 3, wherein said single crystals are oriented along their respective pseudocubic  $\langle 001 \rangle$  direction.





2-2 Composite Transducer

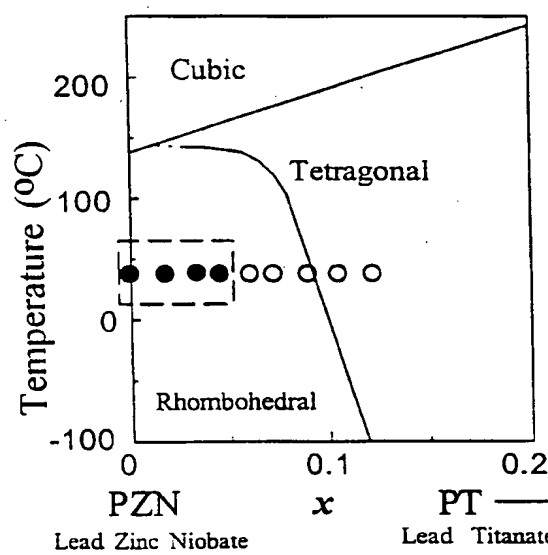
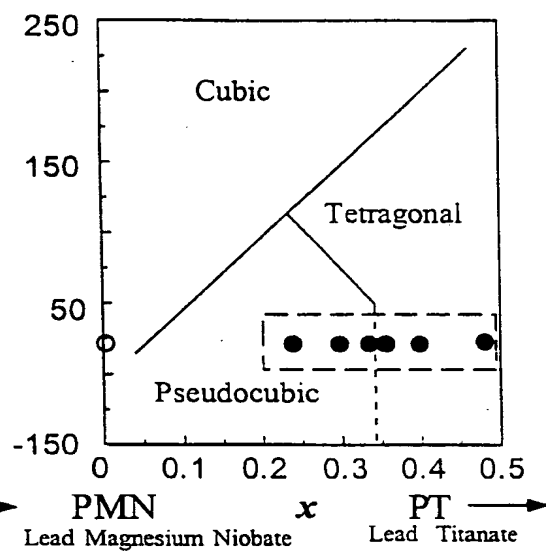
Fig 1a



1-3 Composite Transducer

Fig 1b

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Fig 2aFig 2b

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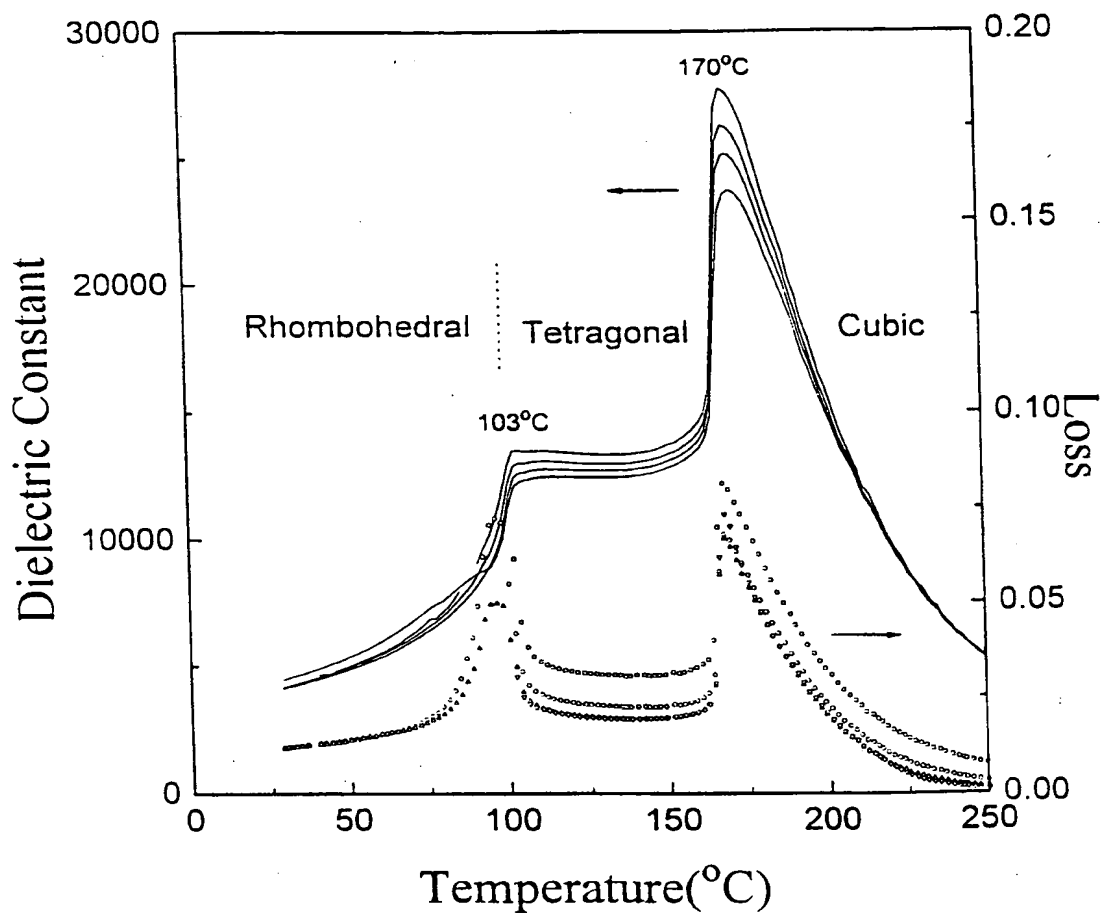


Figure 3

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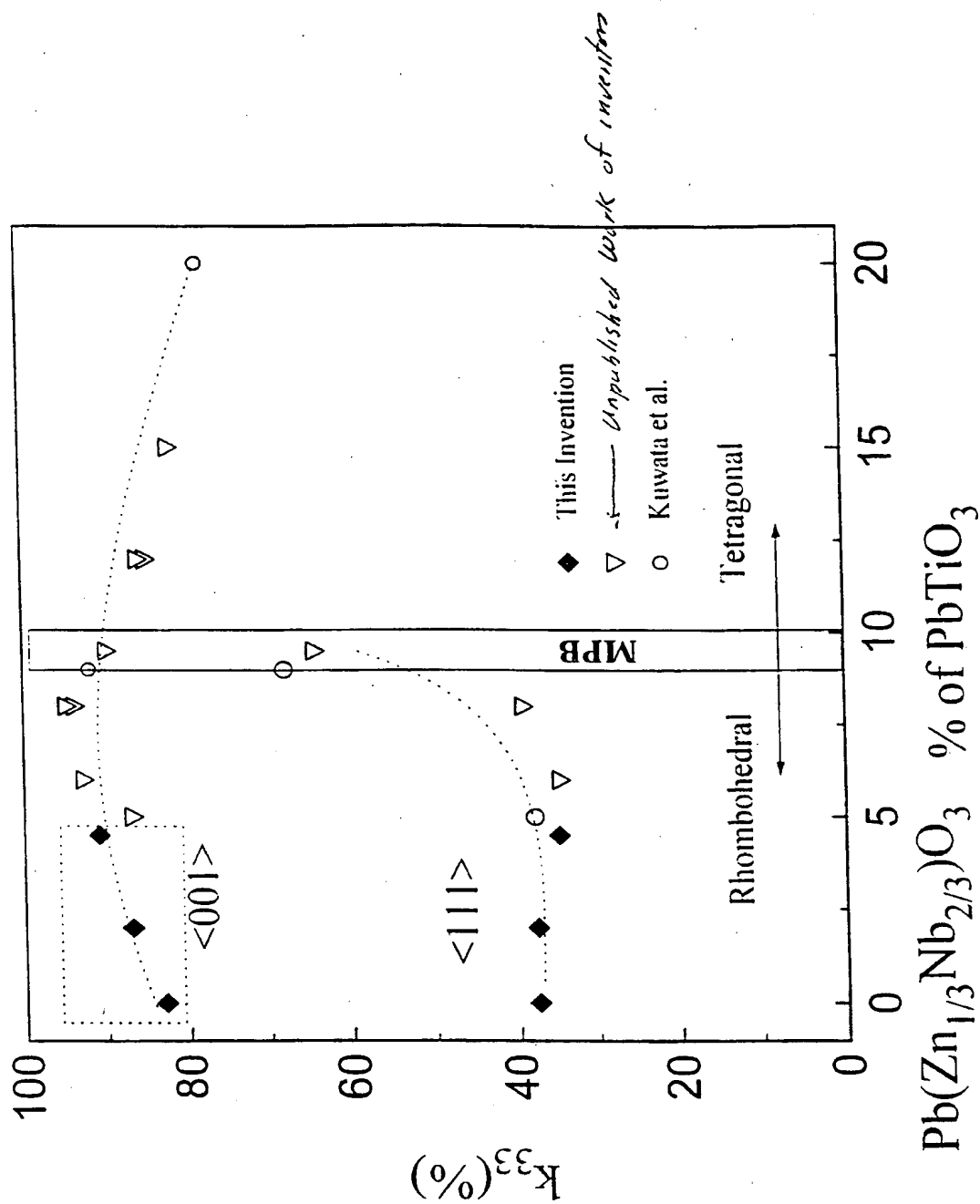


Figure 4

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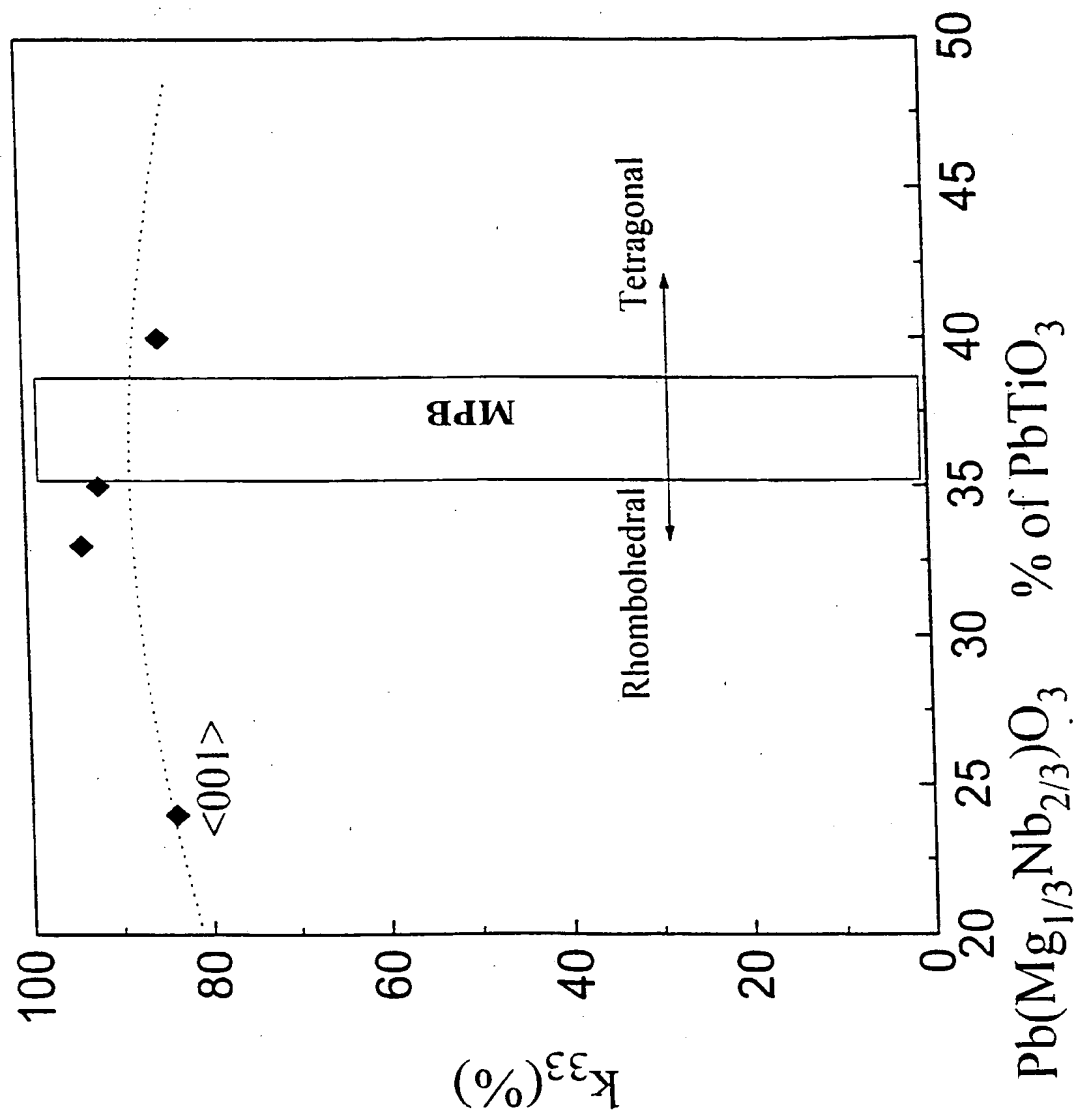
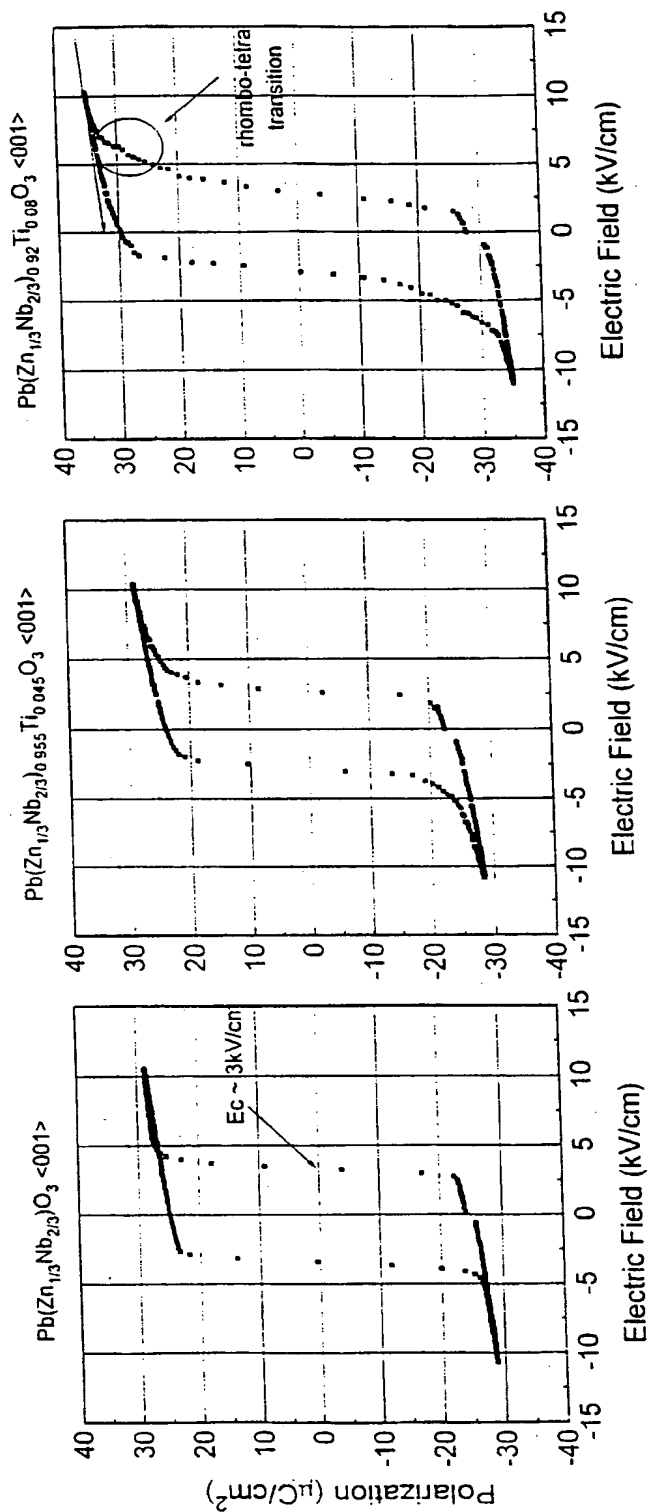


Figure 5

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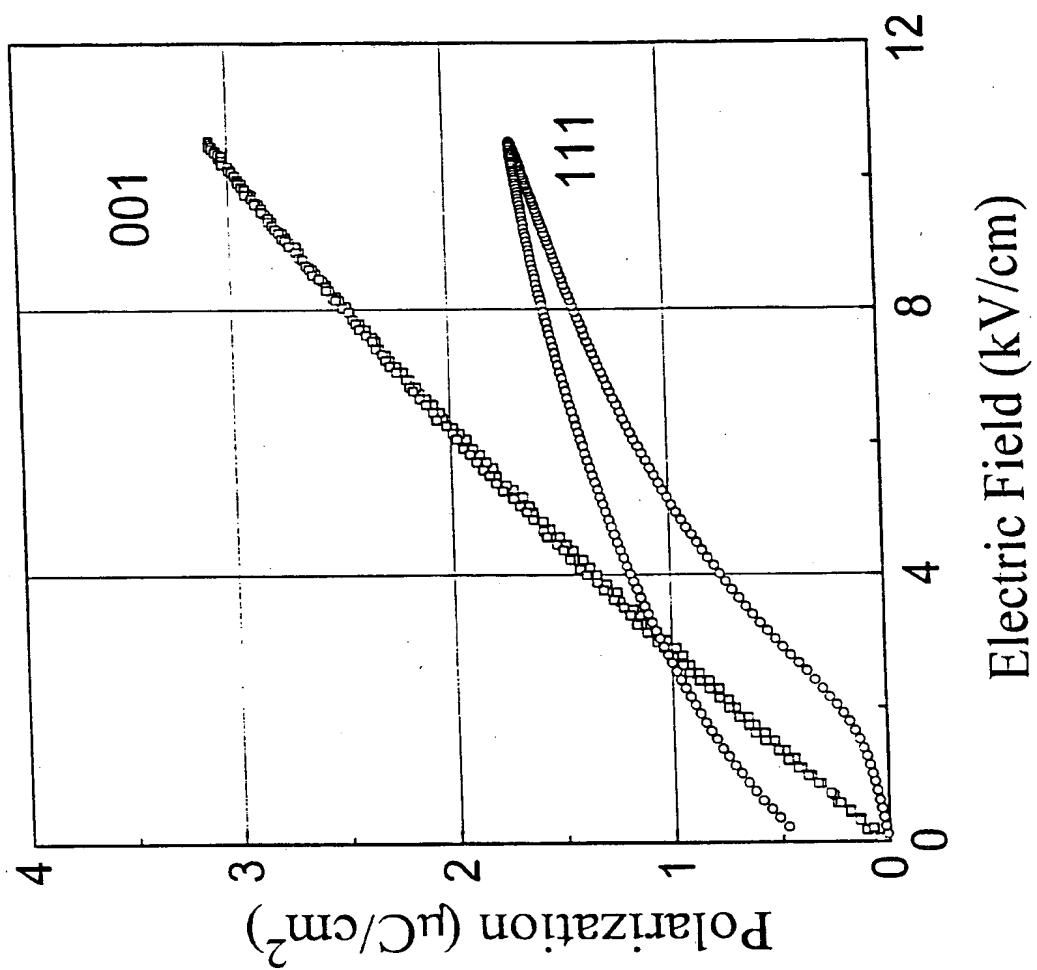


Figure 7

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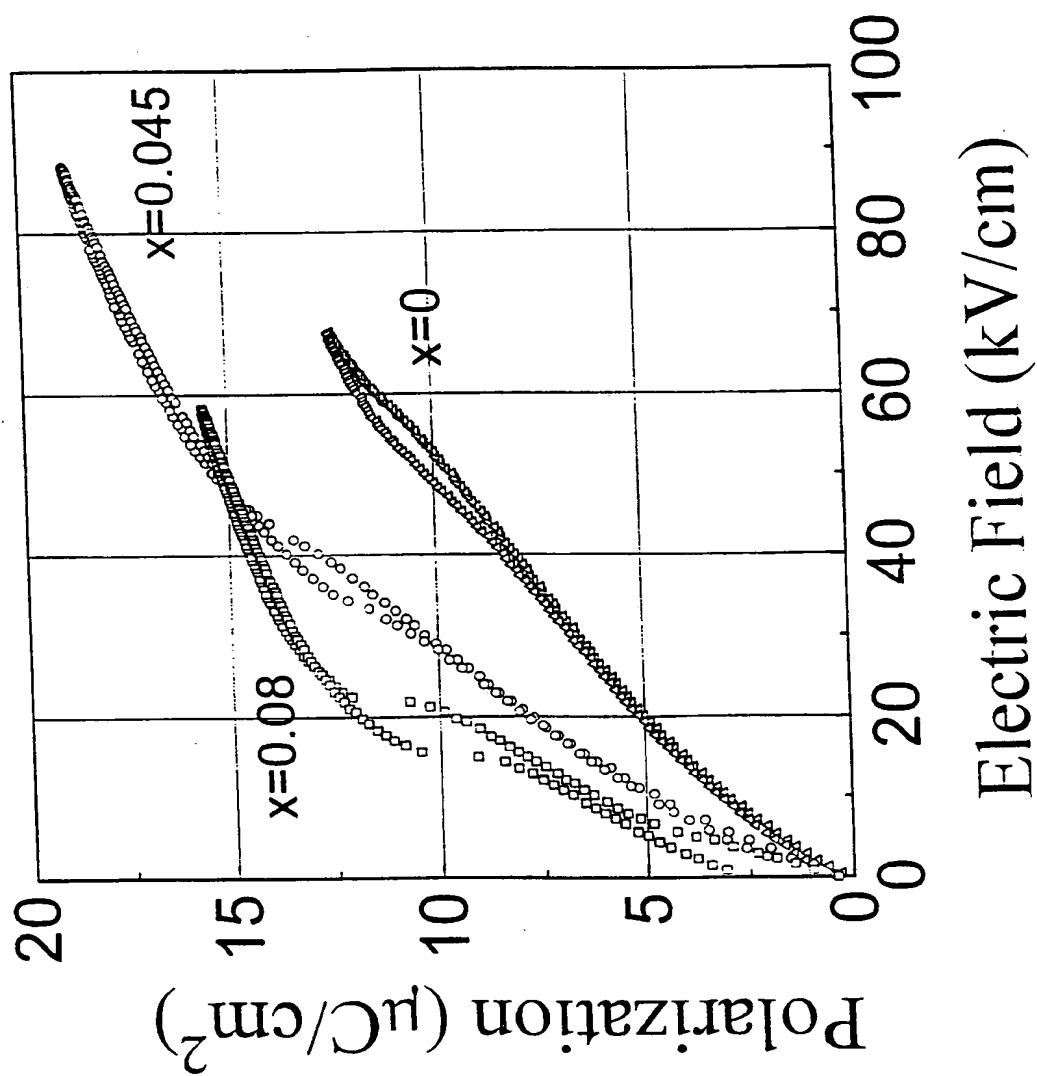


Figure 8



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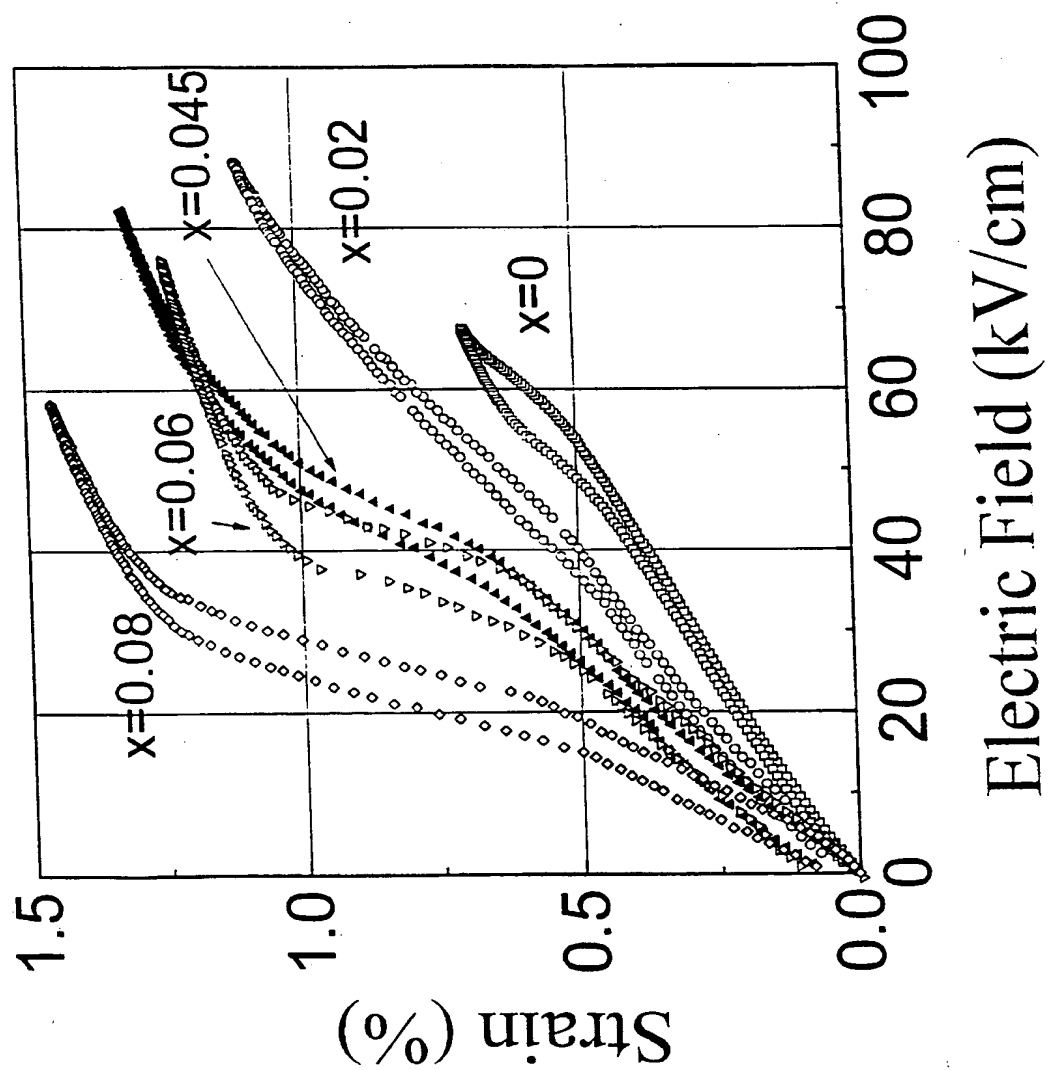


Figure 9

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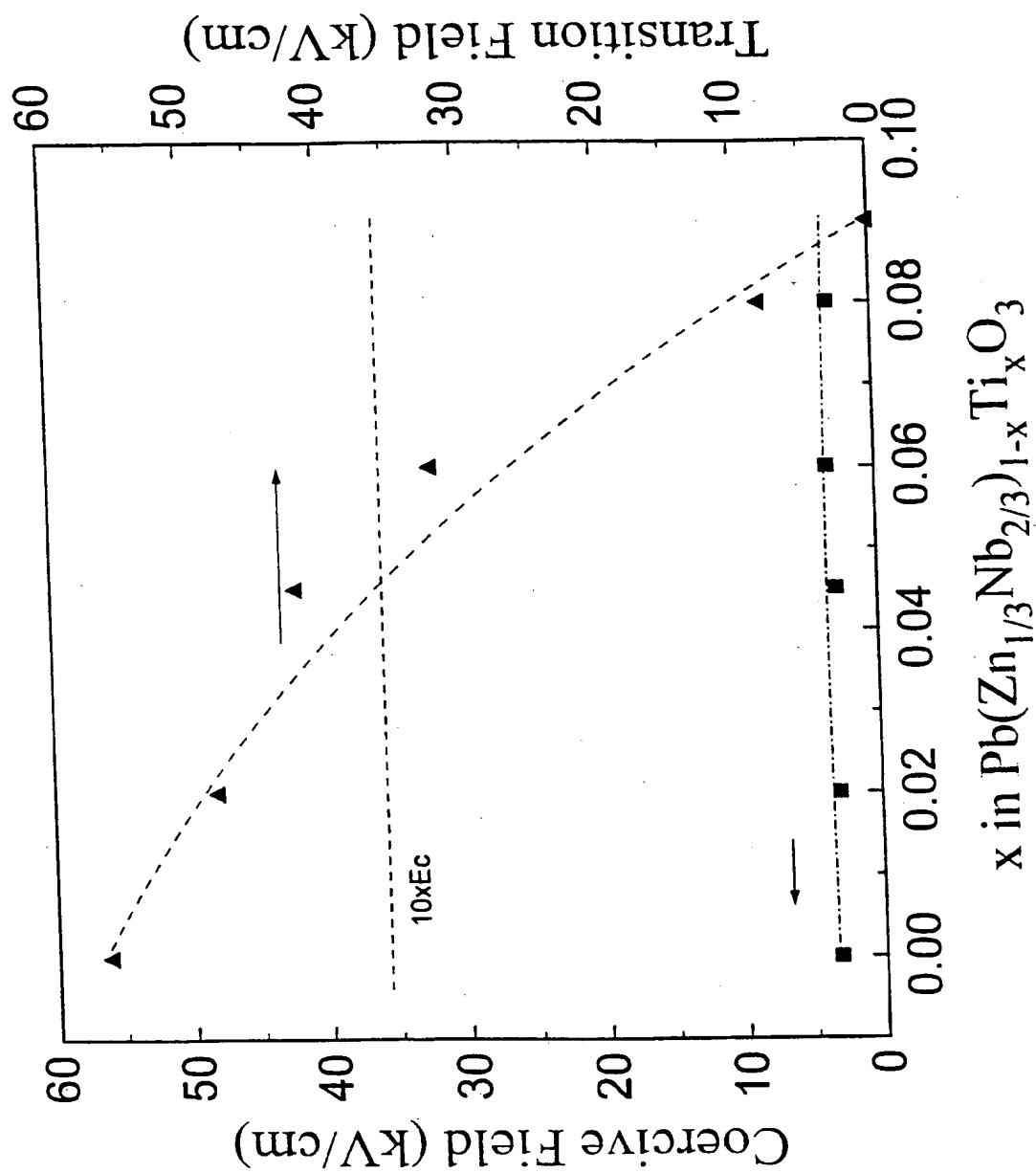


Figure 10

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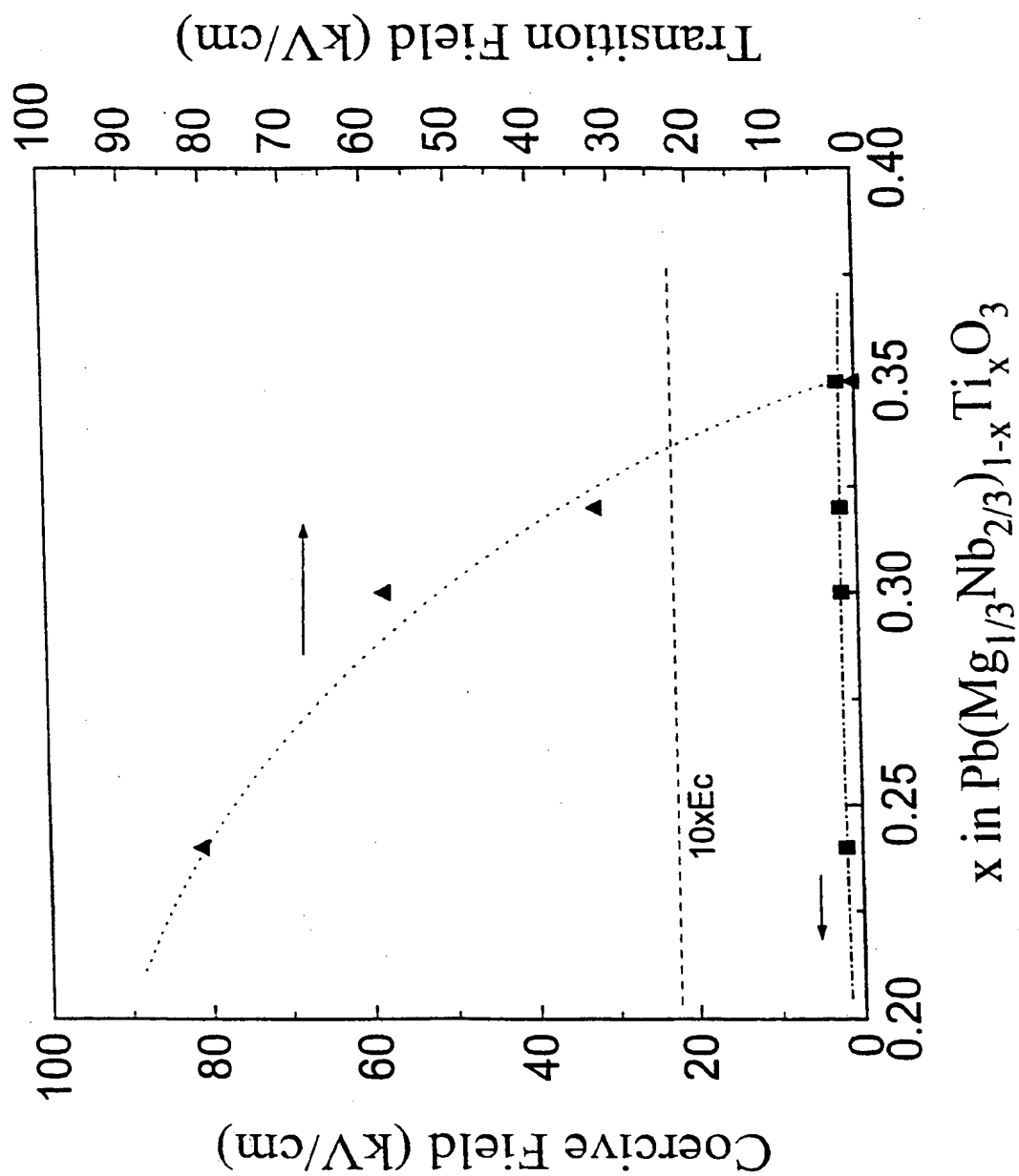
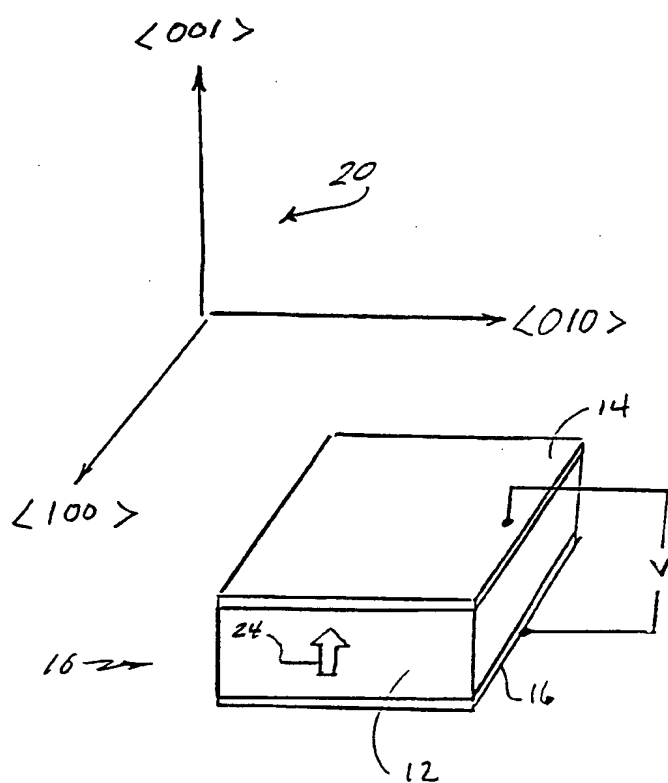
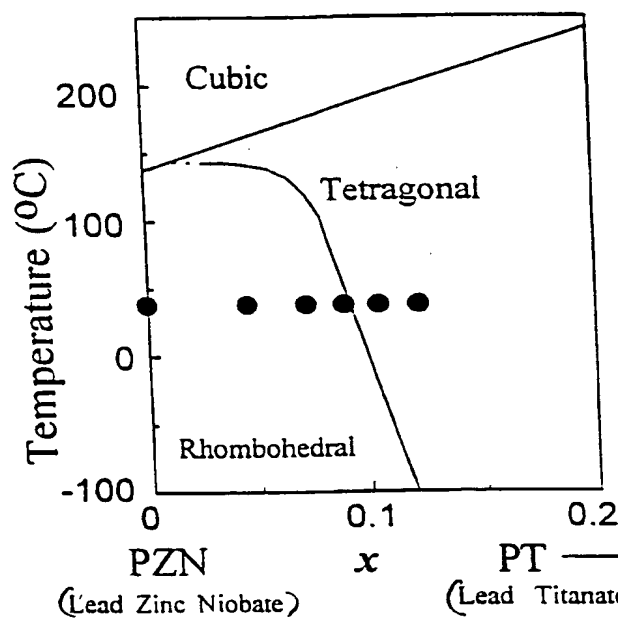
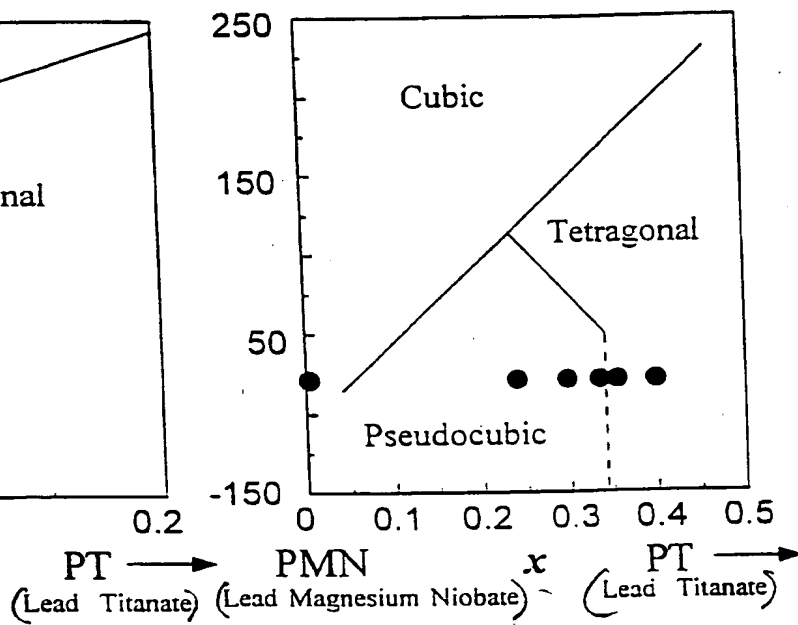


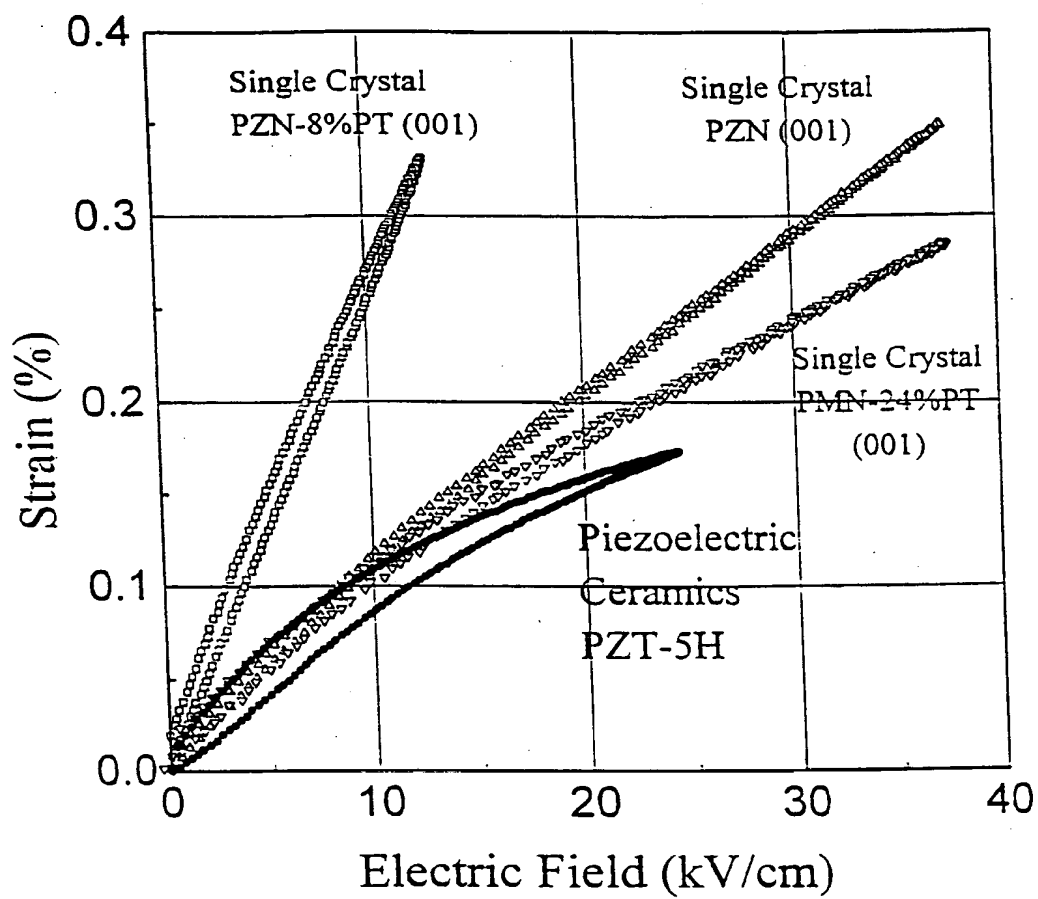
Figure 11

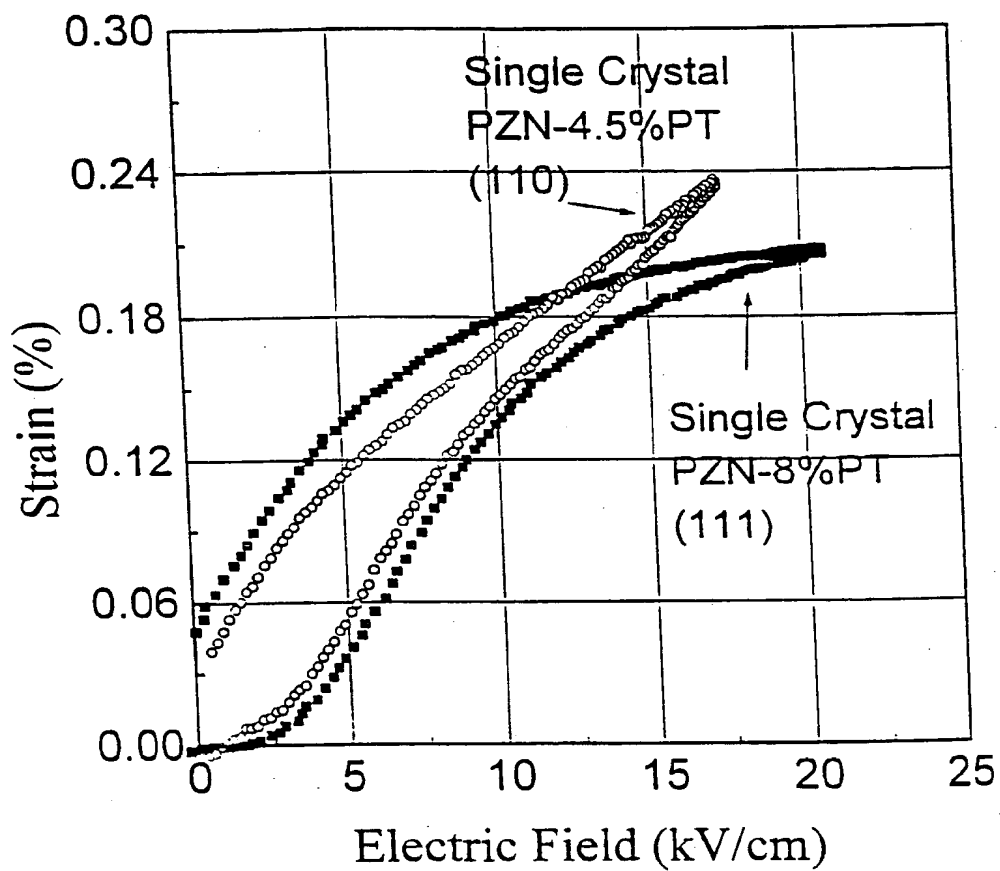
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FIG 12

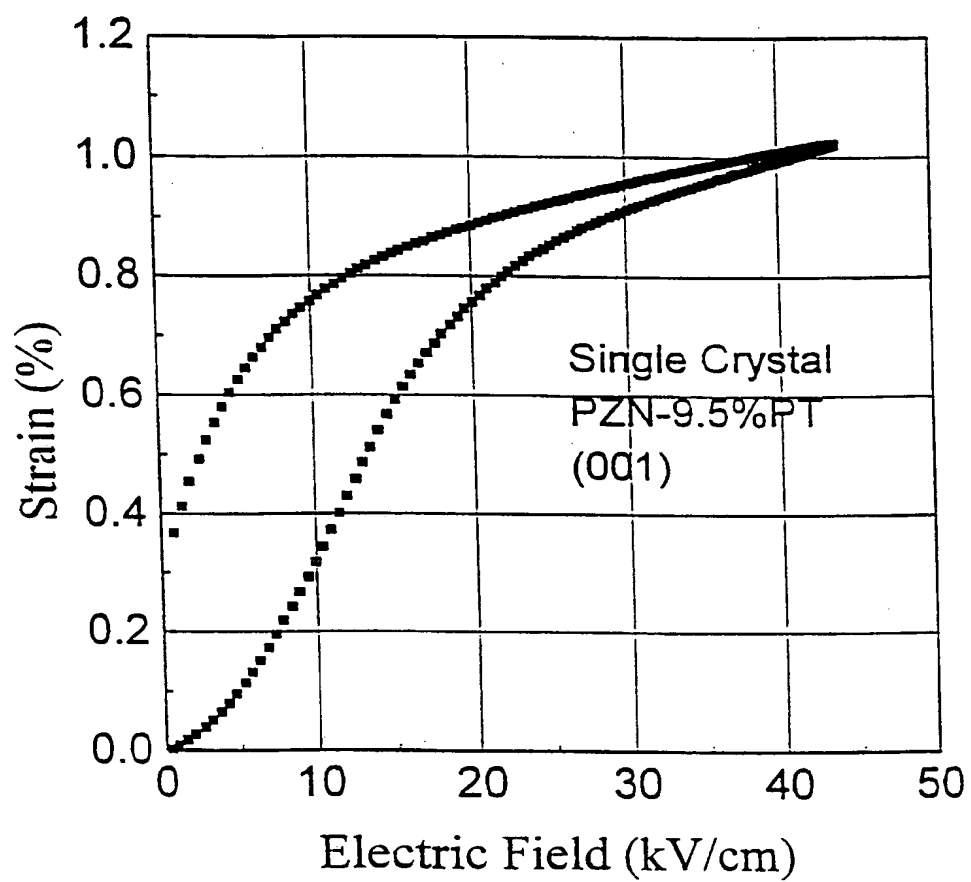
FIG 13aFIG 13b

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FIG 14



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FIG 16



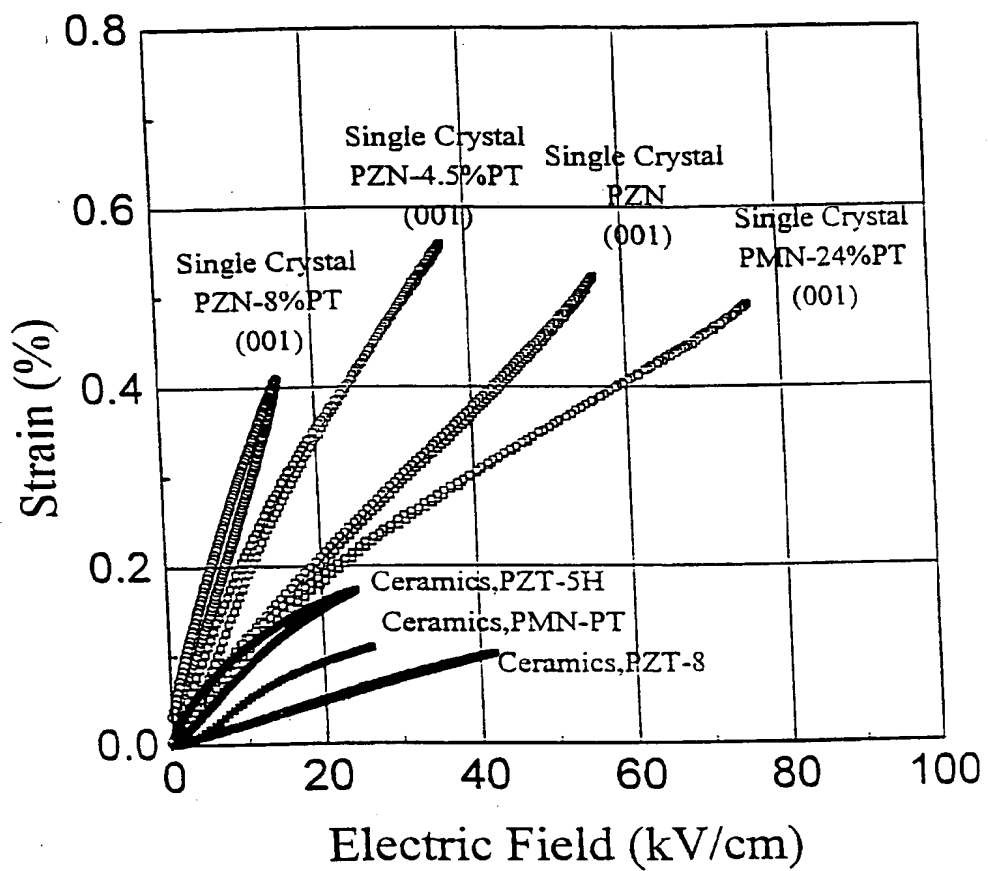
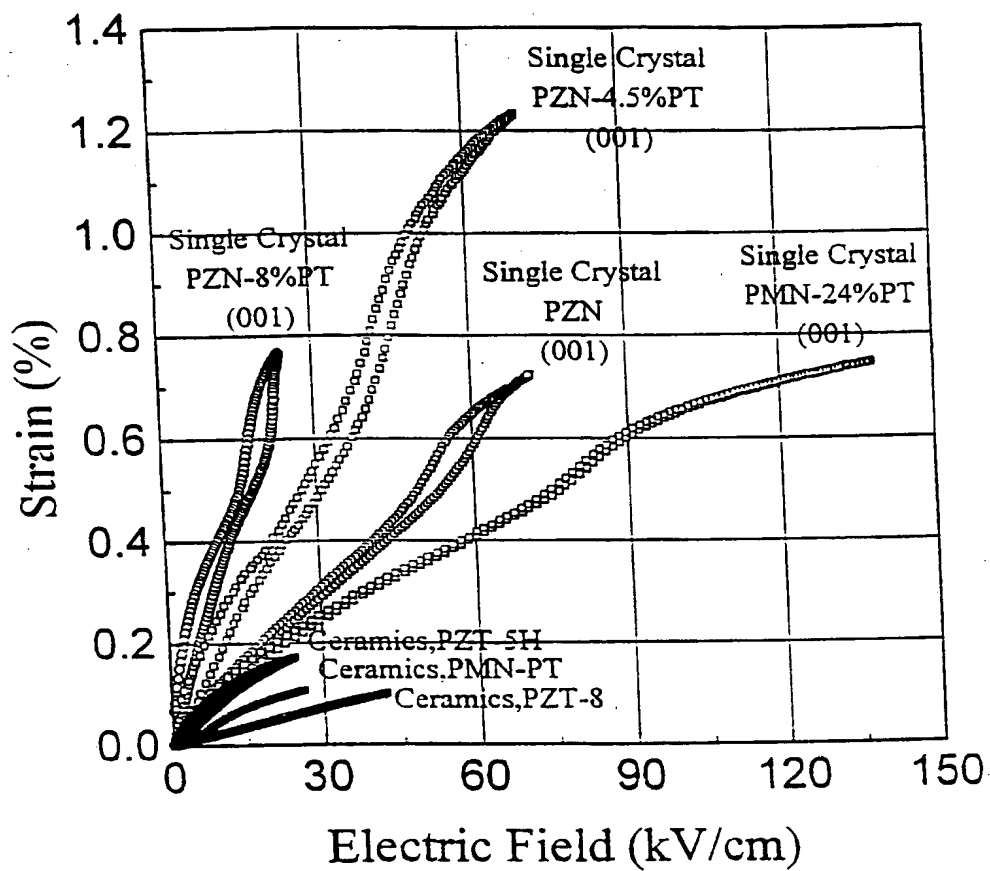
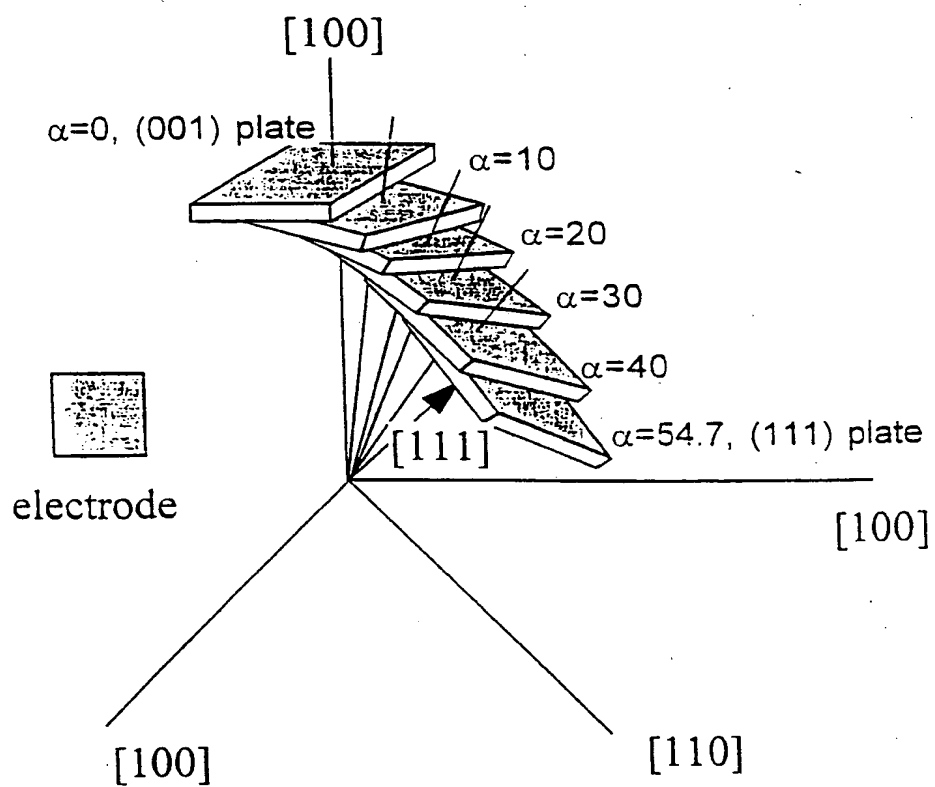


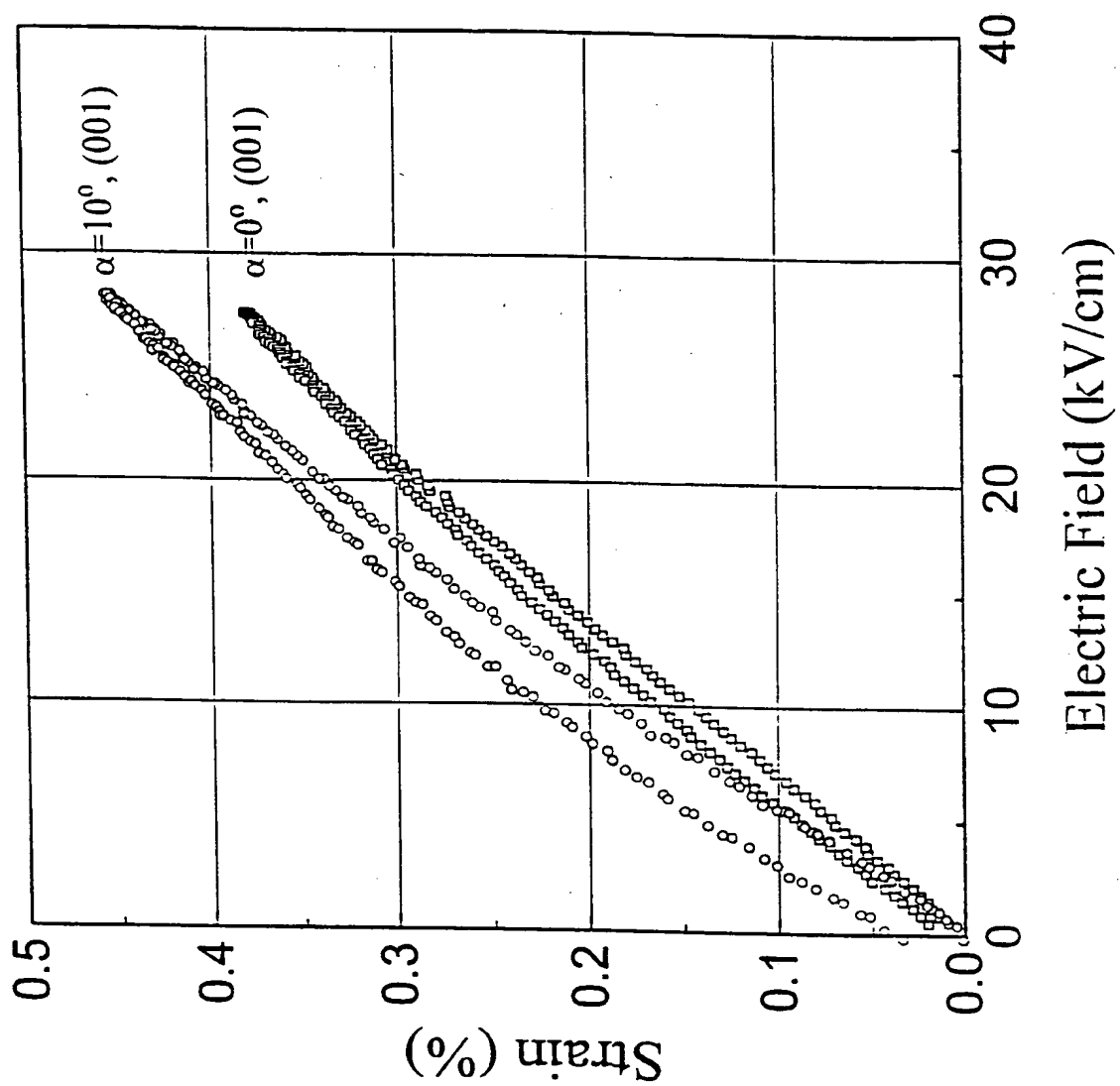
FIG 17

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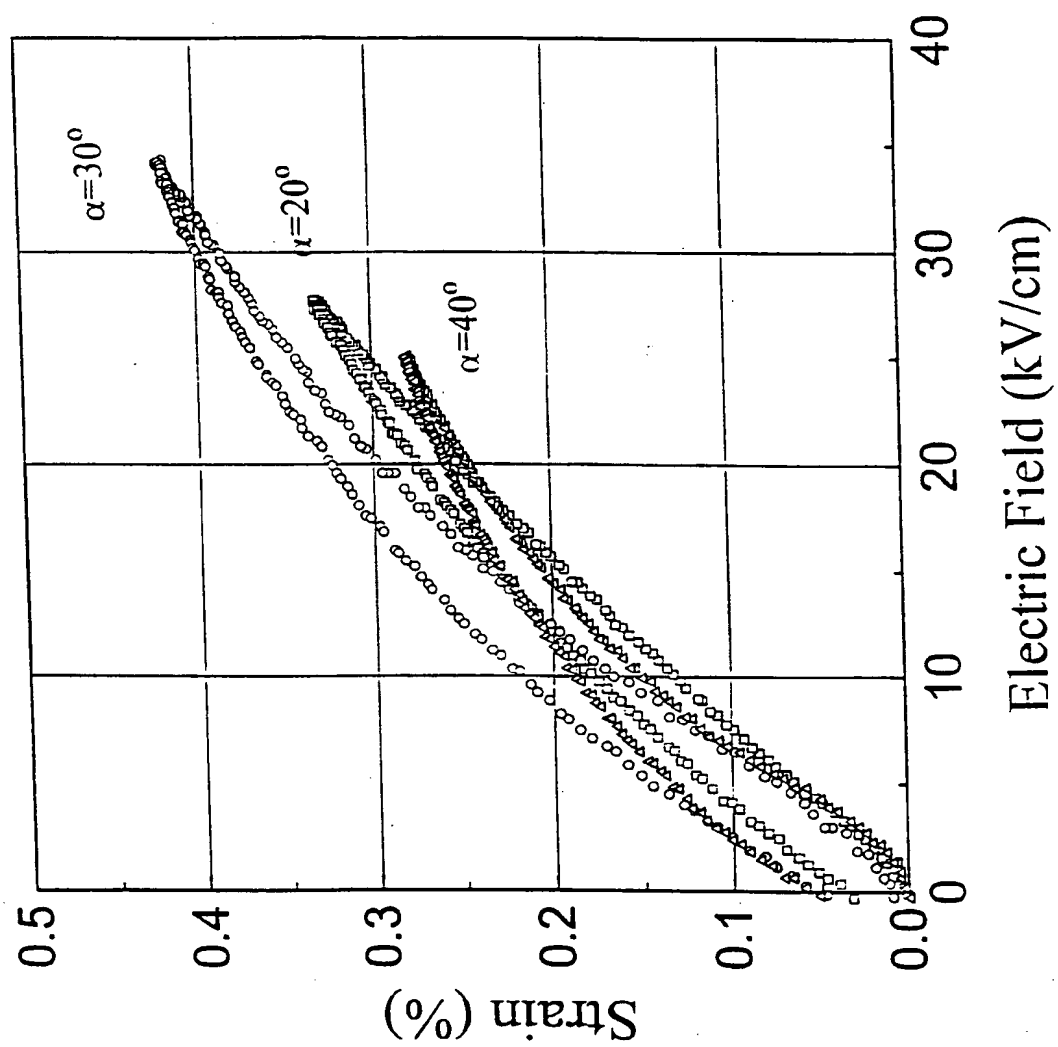
FIG 18

FIG 19

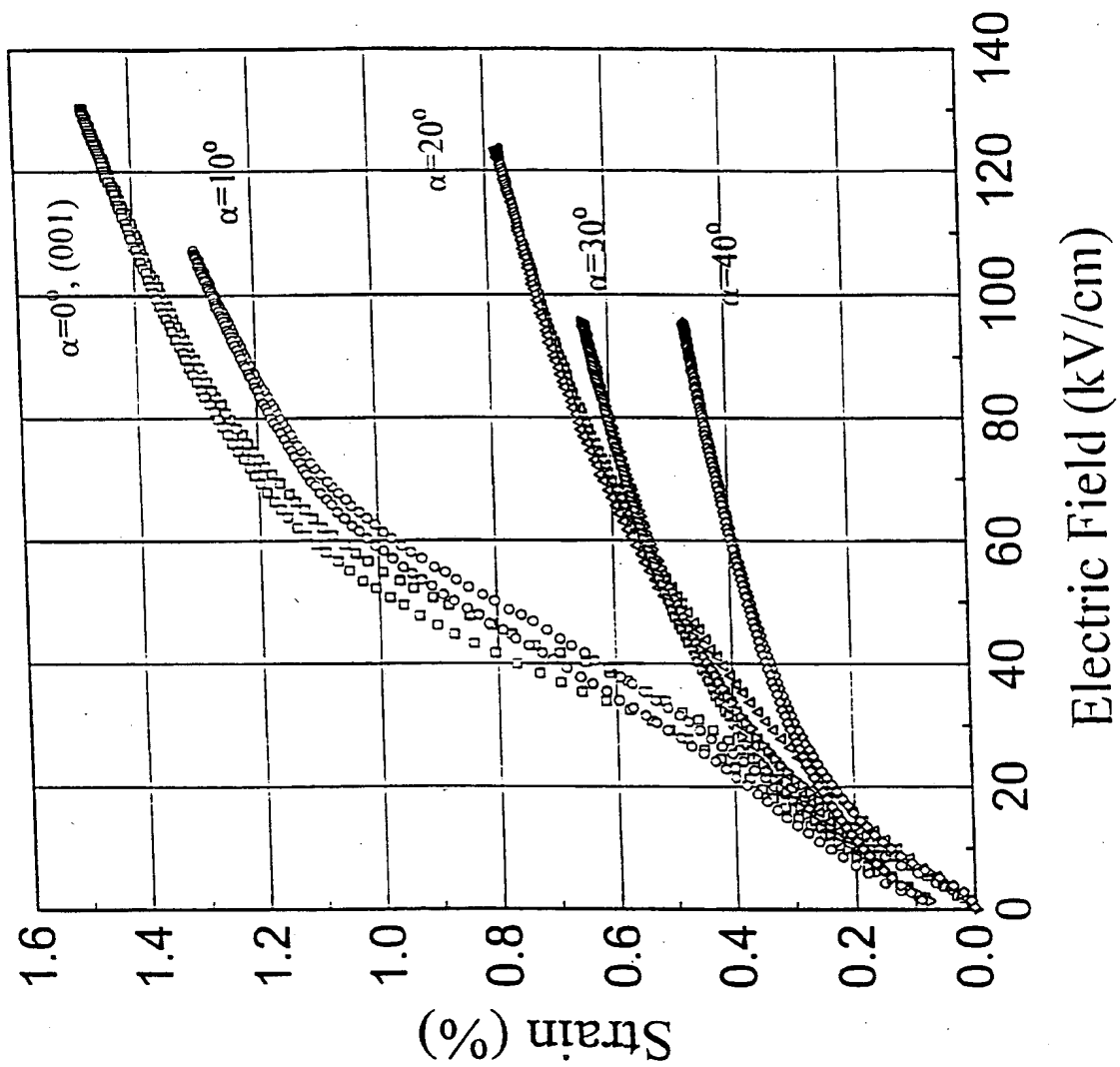
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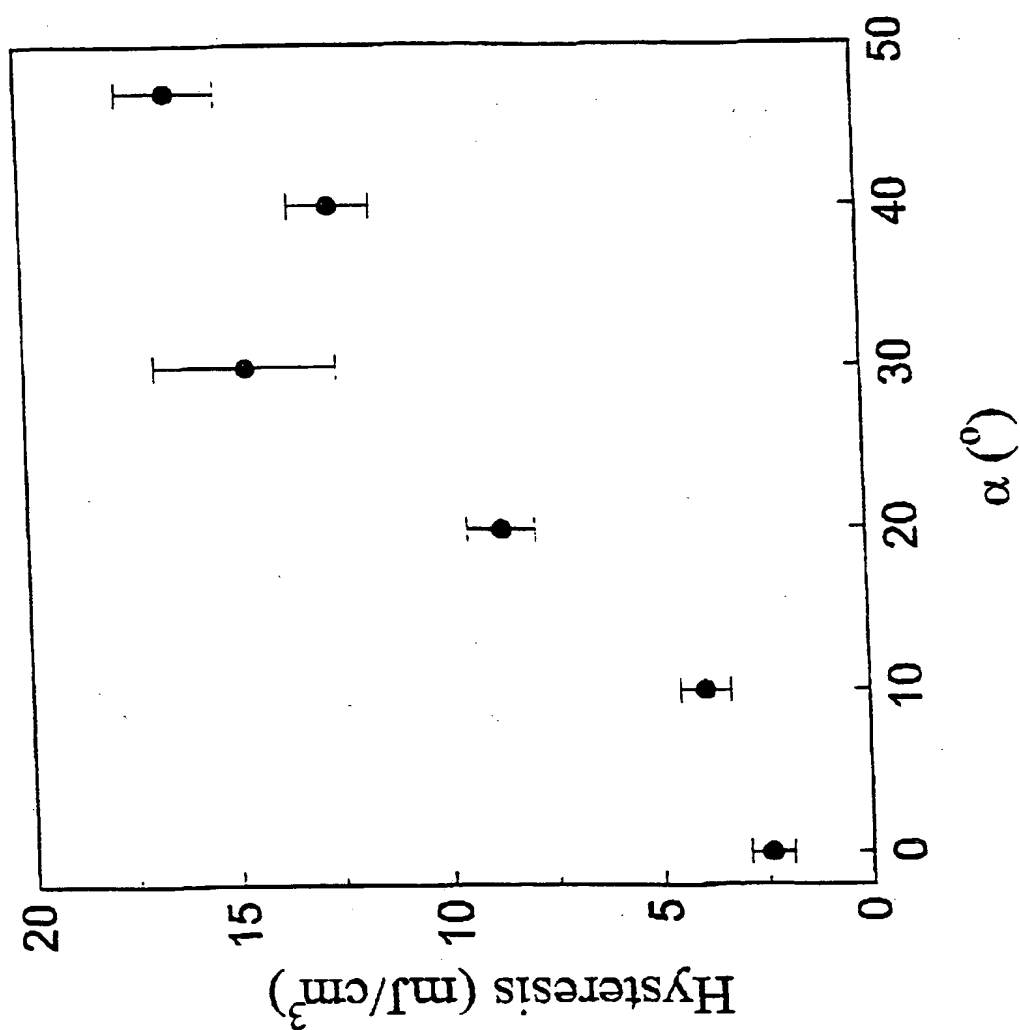
Fig 20

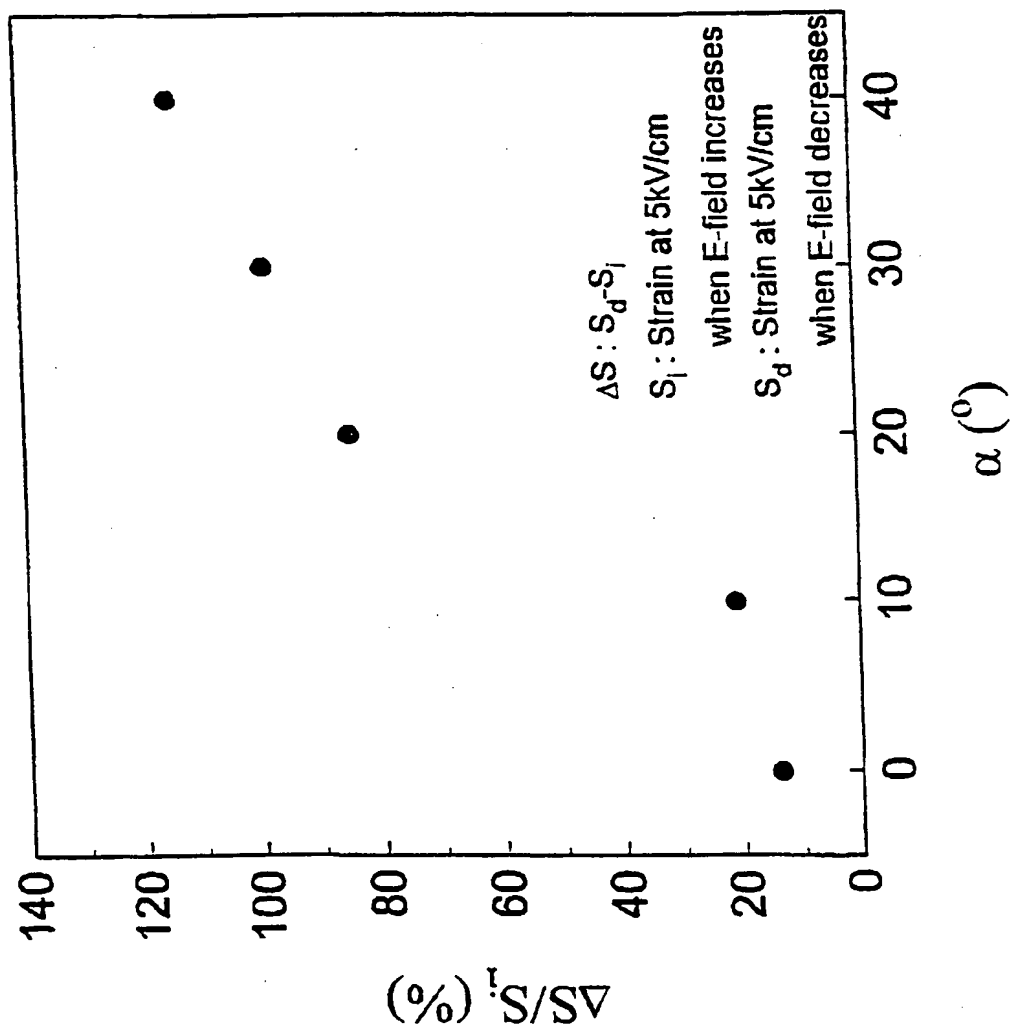
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Figs 21

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Fig 22

Fig 23

FIG 24



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/01521

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01L 41/04

US CL : 310/357,358,313A

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 310/357,358,313A

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, Derwent

crystal, lead magnesium niobate, lead zinc niobate, orientation

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,402,791A (Saitoh et al) 04 April 1995 (04/04/95), entire document, specifically col. 14, lines 29-35.	1-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

16 MARCH 1998

Date of mailing of the international search report

07 MAY 1998

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